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**REMEDIAL INVESTIGATION/FEASIBILITY STUDY
OVERSIGHT AND REVIEW
H.O.D. LANDFILL SITE
ANTIOCH, ILLINOIS**

QUALITY ASSURANCE PROJECT PLAN

**CONTRACT NO. 68-W8-0086
WORK ASSIGNMENT NO. 15-5P2F**

November 18, 1992

Prepared for:

**U.S. ENVIRONMENTAL PROTECTION AGENCY
Region V
Office of Superfund
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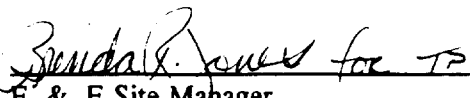
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Work Assignment No. 15-5P2F

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1. PROJECT DESCRIPTION

1.1 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) requires all EPA contractors to participate in a centrally managed quality assurance (QA) program. This requirement applies to all environmental monitoring and measurement efforts mandated or supported by EPA.

Each contractor that generates analytical data is responsible for implementing minimum procedures to assure that the precision, accuracy, completeness, and representativeness of its data are known and documented. To ensure that this responsibility is met uniformly, EPA requires each contractor to prepare a written QA Project Plan (QAPP) for every project that it is contracted to perform.

Ecology and Environment, Inc. (E & E), has been tasked by EPA to provide technical oversight of the Remedial Investigation/Feasibility Study (RI/FS) activities conducted by a potentially responsible party (PRP), Waste Management of Illinois, Inc. (WMII), and its consultant, Warzyn, Inc. (Warzyn), at the H.O.D. Landfill site. RI/FS activities will be conducted at the site, which is located in Antioch, Illinois. E & E will conduct all work on this assignment pursuant to Work Assignment No. 15-5P2F under Alternative Remedial Contracting Strategy (ARCS) Contract No. 68-W8-0086.

EPA issued an Administrative Order on Consent for the H.O.D. Landfill site on August 20, 1990. WMII is the only PRP agreeing to the consent order and is therefore referred to as the Respondent. The Administrative Order requires the Respondent to, among other tasks, fully determine and quantify the nature and extent of the contamination associated with the site.

Field activities to be performed by the consultant include the collection of soil, sediment, leachate, groundwater, and surface water samples from locations thought to be

contaminated based on past site activities. E & E's support in this project will include oversight of all field activities conducted by the consultant, obtaining portions of 10 percent of the total number of samples of each matrix (or at least one sample per matrix) collected by the consultant (including duplicates and matrix spike/matrix spike duplicates [MS/MSD]), technical review of documents and analytical data, review of the Respondent's Risk Assessment (RA), evaluation of the Respondent's compliance with the terms of the Administrative Order, and preparation of biweekly trip reports summarizing the field activities.

This QAPP incorporates requirements concerning the following activities:

- Sample collection and chain-of-custody;
- Document control;
- Laboratory instrumentation, analysis, and control; and
- Review of all project deliverables.

1.2 SITE BACKGROUND

The H.O.D. site is an inactive landfill located within the eastern boundary of the village of Antioch, Lake County, Illinois. The site consists of a total of 80 acres, 51 of which have been landfilled. The old landfill, consisting of 24.2 acres and situated on the western one-third of the site, operated between 1963 and 1975. The new landfill, consisting of 26.8 acres and situated east of the old landfill, operated between 1975 and 1984. The combined landfill accepted both municipal waste and a variety of industrial and special wastes. Figure 1-1 shows the site location and Figure 1-2 shows the site features.

1.3 SITE HISTORY

See the H.O.D. site work plan (WP) (E & E 1990) and Addendum 1 to the site WP submitted with this QAPP for a complete discussion of the site history.

1.4 SUMMARY OF OVERSIGHT ACTIVITIES

As part of its oversight responsibilities, E & E will obtain, as oversight samples, 10 percent (or a minimum of one sample per matrix) of the total number of samples collected by the consultant. These samples will provide confirmatory analytical results that will be used to enlarge EPA's data base and to check on the sampling and analytical procedures used by the

Respondent and its laboratory as an external QA measure. This QAPP presents the procedures that will be implemented by E & E in the collection and analysis of these oversight samples. The number, analytical methods, and general collection locations of the samples are described in Section 4 of this QAPP.

The samples collected by E & E will be submitted to an EPA Contract Laboratory Program (CLP) laboratory. CLP supports EPA's Superfund effort by providing a range of state-of-the-art chemical analysis services of known quality on a high-volume, cost-effective basis. It fulfills the basic requirement of providing legally defensible analytical results for use in supporting EPA's enforcement actions.

The oversight samples will be submitted for analysis for Target Compound List (TCL) compounds, Target Analyte List (TAL) analytes, and several general chemistry parameters. The general chemistry analyses will be submitted to a CLP laboratory as Special Analytical Services (SAS) requests. See Table 1-1 for a summary of the oversight samples that E & E will collect and the analyses that will be performed.

The required detection limits for the TCL compounds and TAL analytes to be analyzed for are presented in Appendix A (including the drinking water TCL/TAL lists). Accuracy and precision requirements for CLP protocol TCL and TAL analyses are described in the current Statement of Work (SOW) for Organics Analysis (CLP SOW OLM01) and the SOW for Inorganic Analysis (ILM01). Detection limits, as well as the required accuracy and precision requirements for the general chemistry parameters, are described in the SAS requests presented in Appendix B.

A compliance QA program has been incorporated into all aspects of CLP operation. The specific laboratory or laboratories that will provide the chemical analysis of the samples will be determined by the Region V Sample Management Office (SMO) prior to the collection of samples.

1.5 PROJECT OBJECTIVES

Based on E & E's understanding of present conditions at the site and the requirements set forth in the Consent Order, the primary objectives of collecting RI/FS oversight samples are as follows:

- provide confirmatory analytical results of the Respondent's data;
- enlarge EPA's data base for the site; and
- ensure compliance of the Respondent's consultant with all applicable plans and documents.

1.6 INTENDED DATA USAGE AND DATA QUALITY OBJECTIVES

The data collected during the RI oversight will be used to confirm the conclusions of the Respondent's Risk Assessment and other RI/FS documents. Data quality objectives (DQOs) are qualitative and quantitative statements that specify the quality of the data required to support decisions made during RI/FS activities and are based on the end uses of the data. As such, different data uses may require different levels of data quality. The five analytical levels that address various data uses and the Quality Control (QC)/QA effort and methods required to achieve the desired level of quality are outlined below:

- DQO Level I (screening): This level provides the lowest data quality and the most rapid results. It is often used for health and safety monitoring, preliminary results, initial site characterization, and locating areas for further study.
- DQO Level II (field analyses): This level provides rapid results and better quality than Level I. This level may include laboratory-generated data, depending on the level of QC exercised.
- DQO Level III (engineering): This level provides an intermediate level of data quality and is used for site characterization. This may include mobile laboratory and fixed-base laboratory data without the full QC documentation of higher levels.
- DQO Level IV (confirmational): This level provides the highest level of data quality and is used for purposes of risk assessment, engineering design, and cost analyses. These analyses require full CLP analytical and data validation procedures in accordance with EPA-recognized protocols (RAS protocols).
- DQO Level V (non-standard): This refers to analysis by non-standard protocols (SAS protocols). These analyses often require method development or adaptation with QC documentation similar to DQO Level IV.

An important factor in defining whether DQOs have been met involves ensuring that the appropriate analytical level has been used to support the intended data use. The oversight samples collected by E & E will have the DQO levels listed below:

- TCL/TAL - all matrices (except drinking water): DQO Level IV
- TCL/TAL - drinking water samples: DQO Level V (using the SOW for drinking water).
- SAS Requests: DQO Level II.

1.7 PROJECT SCHEDULE

A schedule for the completion of the field investigation oversight and sampling activities is presented in Figure 1-3. This schedule is dependent upon submittal and approval of the Respondent's WP, field sampling plan (FSP), and QAPP. The following assumptions have been made in developing the proposed project schedule.

- The start date will be contingent upon receiving approval of E & E's WP and QAPP (i.e., notice to proceed) from EPA.
- EPA will obtain site access for field investigation activities within a time frame that will not interrupt the proposed schedule.
- EPA personnel will respond to draft submittals within 30 days.
- The majority of the field investigation activities are expected to be performed using Level D protection. Should site conditions warrant extensive upgrading of levels of protection, revisions to the proposed field investigation schedule may be required.
- All field equipment and supplies required for this field investigation will be procured prior to initiating field activities.

Table 1-1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM

Sample Matrix	Laboratory Parameter	Analytical Parameter	Total No. Respondent's Samples ^a	Total No. Oversight Samples	Oversight Field Duplicates	Oversight Field Blanks ^b	Oversight MS/MSD ^{c,d}	Total Oversight Samples ^e
Surface Soil/Sediments	Volatiles	RAS Protocols	5	1	1	--	1	2
	Semivolatiles	RAS Protocols	5	1	1	--	1	2
	Pesticides/PCBs	RAS Protocols	5	1	1	--	1	2
	Metals	RAS Protocols	5	1	1	--	1	2
	Cyanide	RAS Protocols	5	1	1	--	1	2
	TOC ^f	SAS - MSA II	5	1	1	--	1	2
Leachate	Volatiles	RAS Protocols	5	1	1	1	1	3
	Semivolatiles	RAS Protocols	5	1	1	1	1	3
	Pesticides/PCBs	RAS Protocols	5	1	1	1	1	3
	Metals	RAS Protocols	5	1	1	1	1	3
	Cyanide	RAS Protocols	5	1	1	1	1	3
	Chloride	SAS - EPA 325	5	1	1	1	--	3
	Sulfate	SAS - EPA 375	5	1	1	1	--	3
	Alkalinity	SAS - EPA 310.1	5	1	1	1	--	3
	Total Hardness	SAS - EPA 130	5	1	1	1	--	3

Key at end of table.

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Table 1-1								
SUMMARY OF SAMPLING AND ANALYSIS PROGRAM								
Sample Matrix	Laboratory Parameter	Analytical Parameter	Total No. Respondent's Samples ^a	Total No. Oversight Samples	Oversight Field Duplicates	Oversight Field Blanks ^b	Oversight MS/MSD ^{c,d}	Total Oversight Samples ^e
Leachate (Cont.)	Nitrate-Nitrite Nitrogen and Nitrite Nitrogen	SAS - EPA 353	5	1	1	1	--	3
	Ammonia - Nitrogen	SAS - EPA 350	5	1	1	1	--	3
	TOC ^f	SAS - EPA 415.1	5	1	1	1	--	3
	TDS ^g	SAS - EPA 160.1	5	1	1	1	--	3
Groundwater (monitoring wells)	Volatiles	RAS Protocols	16	2	2	1	1	5
	Semivolatiles	RAS Protocols	16	2	2	1	1	5
	Pesticides/PCBs	RAS Protocols	16	2	2	1	1	5
	Metals ^h	RAS Protocols	16	2	2	1	1	5
	Cyanide	RAS Protocols	16	2	2	1	1	5
	Alkalinity	SAS - EPA 310.1	16	2	2	1	--	5
	Chloride	SAS - EPA 325	16	2	2	1	--	5
	Hardness	SAS - EPA 130	16	2	2	1	--	5
	Sulfate	SAS - EPA 375	16	2	2	1	--	5

Key at end of table.

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Table 1-1
SUMMARY OF SAMPLING AND ANALYSIS PROGRAM

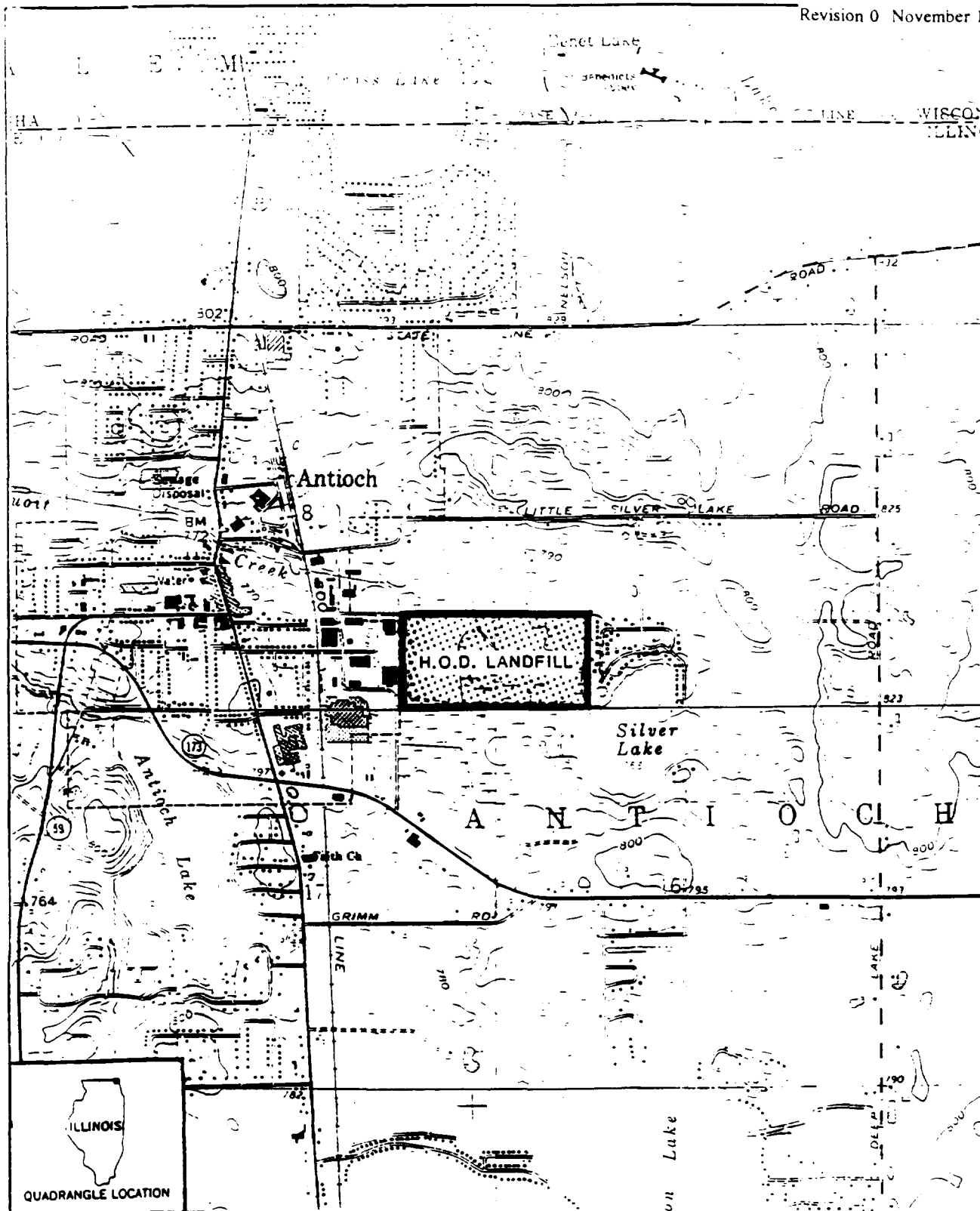
Sample Matrix	Laboratory Parameter	Analytical Parameter	Total No. Respondent's Samples ^a	Total No. Oversight Samples	Oversight Field Duplicates	Oversight Field Blanks ^b	Oversight MS/MSD ^{c,d}	Total Oversight Samples ^e
Groundwater (monitoring wells) (Cont.)	TOC ^f	SAS - EPA 415.1	16	2	2	1	--	5
	TDS ^g	SAS - EPA 160.1	16	2	2	1	--	5
	Nitrate-Nitrite Nitrogen and Nitrite Nitrogen	SAS - EPA 353	16	2	2	1	--	5
	Ammonia - Nitrogen	SAS - EPA 350	16	2	2	1	--	5
Groundwater (municipal private wells)	Volatiles	RAS Protocols	8	1	1	1	1	3
	Semivolatiles	RAS Protocols	8	1	1	1	1	3
	Pesticides/PCBs	RAS Protocols	8	1	1	1	1	3
	Metals	RAS Protocols	8	1	1	1	1	3
	Cyanide	RAS Protocols	8	1	1	1	1	3
Surface Water	Volatiles	RAS Protocols	3	1	1	1	1	3
	Semivolatiles	RAS Protocols	3	1	1	1	1	3
	Pesticides/PCBs	RAS Protocols	3	1	1	1	1	3
	Metals	RAS Protocols	3	1	1	1	1	3
	Cyanide	RAS Protocols	3	1	1	1	1	3

Key at end of table.

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RI/FS Oversight QAPP
H.O.D. Landfill Site
Section 1
Revision 0 November 18, 1992

- a Total number of investigative samples; does not include the number of QC samples.
- b A trip blank is required for volatile organic analysis (VOA) of water samples. One trip blank, which consists of two VOA vials filled with distilled water, will be included with each shipment of VOA water samples.
- c MS/MSD are required for organic analysis. Samples designated for MS/MSD analysis will be collected, with extra volumes at a frequency of one per group or fewer investigative samples. Triple the normal water sample volume will be collected for VOAs and double the normal water sample volumes will be collected for semivolatiles, pesticides, and PCBs.
- d For inorganic analyses, no extra sample volume is required.
- e The number of samples to be collected for MS/MSD and the number of trip blanks are not included in the matrix total.
- f TOC: total organic carbon.
- g TDS: total dissolved solids.
- h Groundwater samples collected from monitoring wells for metals analysis will be field-filtered prior to the addition of preservative.



SOURCE: Ecology and Environment, Inc. 1989; BASE MAP: USGS, Antioch, IL Quadrangle, 7.5 Minute Series, 1960.



FIGURE 1-1 SITE LOCATION

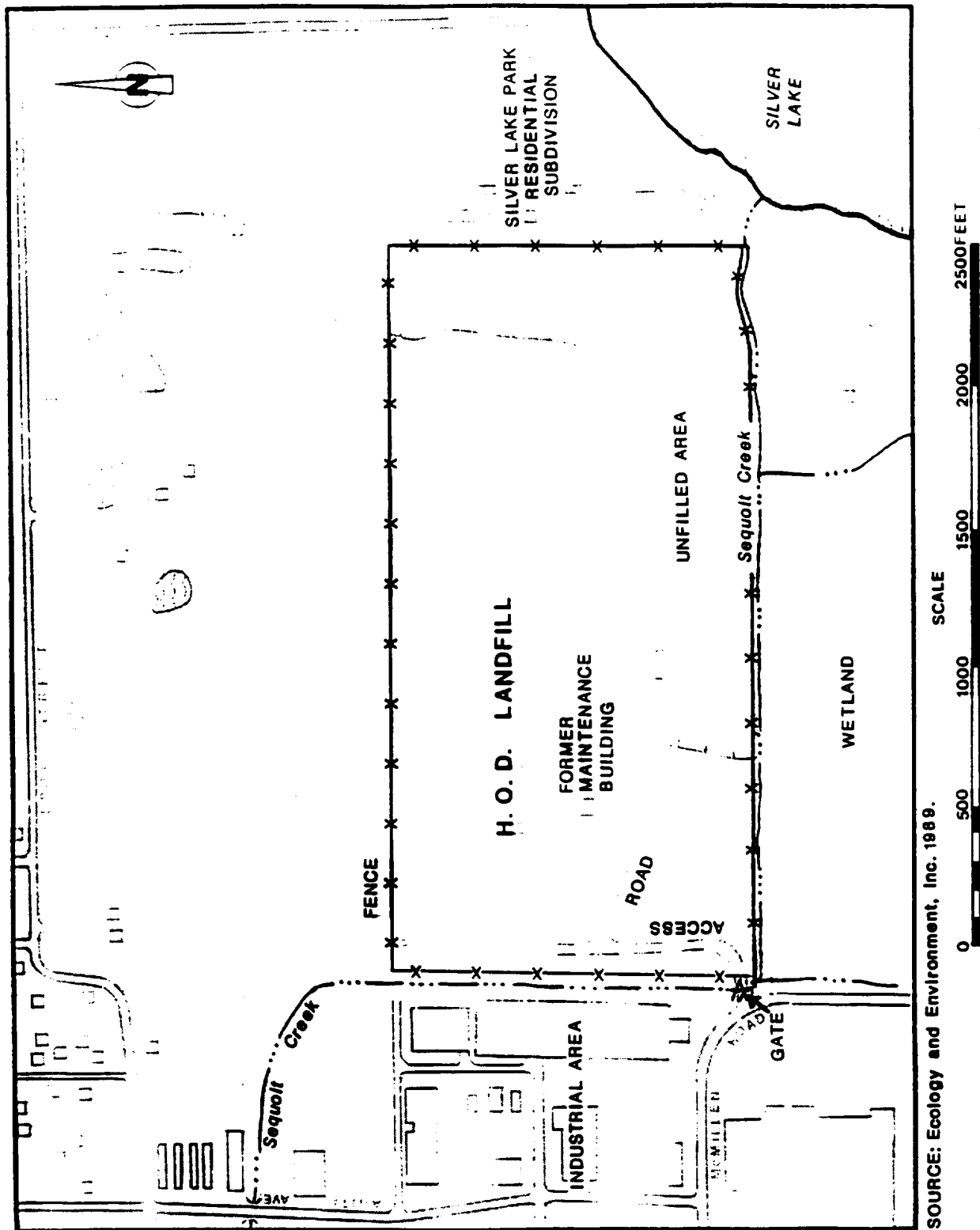


FIGURE 1-2 SITE FEATURES

<p align="center">Figure 1-3</p> <p align="center">PROJECT SCHEDULE</p>			
Task	Description	Starting Date	Due Date (Number of Business Days)
1	Project Planning (Work Plan Addendum)	Acceptance of Work Assignment (October 19, 1992)	November 18, 1992
1.1	QA Project Plan	October 19, 1992	November 18, 1992
2	Background Review	Receipt of Background Information	None
3	Oversight of Fieldwork and Split Sampling	To be Determined ^a	To be Determined ^a
4	Review of Respondent's Documents		
4.1	Review of Project Planning Documents	Receipt of Documents	15 ^b
4.2	Review of Technical Memoranda	Receipt of Documents	15 ^b
4.3	Review of Risk Assessment	Receipt of Document	15
4.4	Review of RI Report	Receipt of Document	15
4.5	Review of FS Documents	Receipt of Documents	15 ^a
5	ROD Support	Upon notice from EPA RPM	To Be Determined
6	Project Management	Upon approval of partial Work Plan	Intermittent Activity

^a Contingent upon approval of the consultant's WP, FSP, and QAPP.

^b Or other mutually agreed-upon time period in the event of concurrent document reviews.

2. PROJECT ORGANIZATION AND RESPONSIBILITIES

E & E is responsible for oversight of field activities performed by the Respondent, review of Respondent-generated documents (as directed by EPA), and preparation of the trip reports. Figure 2-1 shows the project organization.

ARCS Program Manager. The program manager for this project is Thomas Yeates. The program manager has overall responsibility for ensuring that the project meets EPA objectives and E & E quality standards. In addition, he is responsible for technical quality control (QC) and project oversight, and will provide the site manager with access to corporate management.

E & E Site Manager. The E & E Site Manager is Thomas Pachowicz. He is responsible for implementing the project and has the authority to commit the resources necessary to meet project objectives and requirements. The Site Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The Site Manager will report directly to the EPA Region V Remedial Project Manager (RPM), Fredrick Micke, P.E., and will serve as the primary point of contact and control for matters concerning the project. Specifically, the Site Manager will:

- Define project objectives and develop a detailed work plan and schedule;
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task;
- Acquire and apply technical and corporate resources as needed to ensure performance within budget and schedule constraints;
- Monitor and direct field activities to ensure that work performed complies with approved documents;

- Develop and meet ongoing project and/or task staffing requirements, including mechanisms to review and evaluate each task product;
- Review the work performed on each task to ensure its quality, responsiveness, and timeliness;
- Review and analyze overall task performance with respect to planned requirements and authorizations;
- Approve all external reports (deliverables) before their submission to EPA Region V;
- Ultimately be responsible for the preparation and quality of interim and final reports; and
- Represent the project team at meetings and public hearings.

E & E Quality Assurance Officer. The Site Quality Assurance Officer (QAO) is Jerome Oskvarek. The QAO will remain independent of direct job involvement and day-to-day operations, but will have direct access to corporate management as necessary to resolve any QA dispute. He is responsible for auditing the implementation of the QA program in conformance with site-specific requirements, E & E policy, and EPA requirements. Specific functions and duties include:

- Conduct QA audits on various phases of the field operations;
- Review and approve QA plans and procedures; and
- Provide QA technical assistance to project staff.

EPA Region V Quality Assurance Officer. The EPA Region V QAO is George Schupp. The QAO has the responsibility to review and approve this QAPP.

Central Regional Laboratory. Analyses of oversight samples will be performed by a CLP laboratory. Arrangements for these analyses will be made with the EPA Central Region Laboratory (CRL) SMO, Region V. CRL will also be responsible for final data validation including review of tentatively identified compounds (TICs).

Remedial Project Manager. The RPM, Fredrick Micke, P.E., has the overall responsibility for this project to set DQOs and to approve deliverables.

Responsibility for external performance and systems audits of CLP laboratories rests with the Quality Assurance Division of EPA's Environmental Monitoring and Support Laboratory (EMSL) in Las Vegas, Nevada.

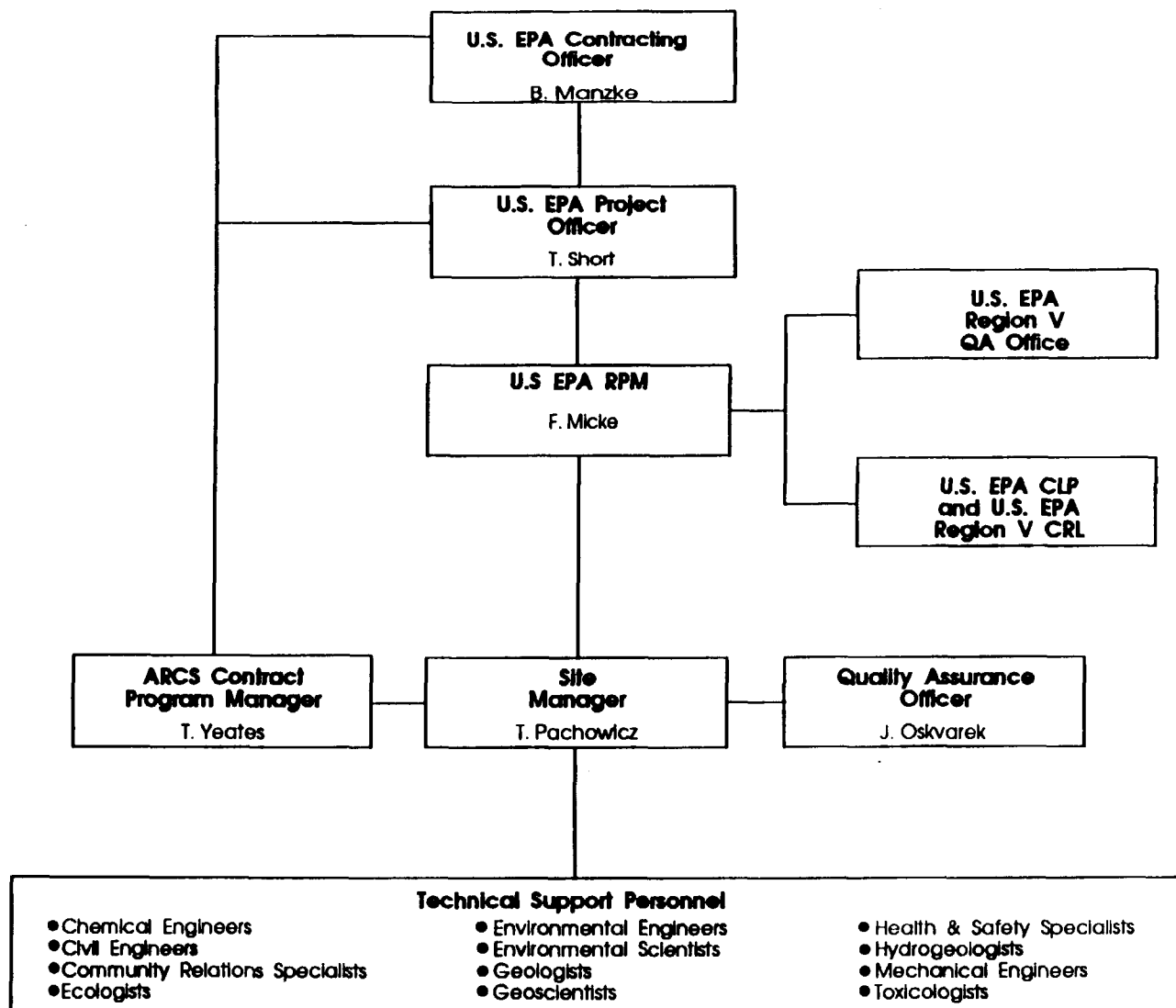


FIGURE 2-1 PROJECT ORGANIZATION CHART FOR H.O.D LANDFILL RI/FS (0)

3. QUALITY ASSURANCE OBJECTIVES FOR ANALYTICAL DATA

The overall quality assurance objective is to ensure that the oversight data are of known and acceptable quality. Data must be sufficiently precise and accurate to be used in a comparison with the data generated by the Respondent's consultant. This oversight sampling program will serve as an external QA measure to check the sampling and analytical procedures of the Respondent and its laboratory.

To achieve the overall DQOs, proper sample handling and analysis and data handling procedures will be followed. These procedures are described in the following sections of this QAPP and are in accordance with the requirements and recommendations of the most recent CLP organic SOW (OLM01) and inorganic SOW (ILM01). This document describes the specific objectives for analytical precision, accuracy, and completeness. The specific objectives for analytical precision, accuracy, and completeness are to achieve the QA acceptance criteria for the proposed analytical procedures. The accuracy, precision, and completeness requirements for RAS analyses are specified in the current versions of OLM01 and ILM01. The sensitivities required for RAS and drinking water SAS analyses will be the contract-required quantitation limits (CRQLs) (Appendix A), also specified in the current organic SOW (OLM01) and inorganic SOW (ILM01). These QA requirements are presented in Exhibit E of both the organic and inorganic CLP SOWs. The accuracy, precision, and sensitivity requirements for CLP SASs are specified in the SAS requests in Appendix B of this QAPP.

Completeness, a measure of the amount of valid data obtained from the measurement system compared to the amount expected under correct conditions, is expected to be 95% or more for CLP data (RAS and SAS). Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling

point, or an environmental condition. The oversight sampling network is designed to provide data that are representative of the Respondent's data and of site conditions. Comparability, a measure of the confidence with which one data set can be compared to another, is achieved by using standard field sampling procedures and recognized laboratory techniques.

To assess whether the overall quality assurance objectives have been met, analyses of specific field quality control samples will be required. These quality control samples include field duplicates, field blanks, and trip blanks. The preparation of these samples is described in Section 4. The frequency with which they will be collected is given in Table 4-1.

Field duplicate results will be used to assess the precision of the sample results. They will be used to monitor overall precision, including the reproducibility of sampling and analytical procedures, as distinct from the precision of analyses of laboratory replicates. Field duplicate samples are collected at a frequency of one per group of 10 or fewer investigative samples per sample matrix.

MS/MSD samples will be collected at a frequency of one per 20 or fewer investigative samples per sample matrix.

Field blank samples will consist of deionized water that has been routed through decontaminated sampling devices, including the filtration device, when appropriate. The field blank samples will be containerized, treated, and handled in the same manner as the oversight samples. Field blanks will be collected at a rate of one for every 10 or fewer samples collected each day.

The trip blank samples will be the responsibility of E & E. They will accompany the water samples to and through the CLP laboratory at a rate of one per shipping container (containing water samples for volatile organic analysis [VOA]) per day.

4. SAMPLING PROCEDURES

Sampling procedures to be used by the Respondent are described in the Sampling and Analysis Plan, Appendix A of the *Quality Assurance Project Plan, Remedial Investigation/Feasibility Study, Volume 1 of 2, H.O.D. Landfill*, prepared by the consultant (Warzyn 1992). E & E will monitor the sampling activities on site. At sampling locations where an oversight sample is required, E & E will provide the consultant with the necessary sample container. The consultant will fill its container and E & E's container simultaneously. E & E will receive the filled oversight sample containers. Any field measurements required will be taken by the Respondent's consultant. E & E will record the results, along with the method used to obtain the results, in a field notebook for the oversight program at the time of sampling.

The bottles used for this sampling effort will be prepared using procedures specified in EPA's *Specifications and Guidance for Obtaining Contaminant-Free Sampling Containers*, (April 1990).

The Respondent's consultant will collect samples from on-site locations for physical testing (i.e., grain size, Atterberg Limits, moisture content, in-place density, and clay mineralogy) and chemical testing. Per EPA's instructions, E & E will collect portions of samples to be analyzed for chemical parameters, and will not collect portions of samples to be analyzed for physical parameters.

Specific locations of the samples collected by the Respondent are presented in the consultant's *Sampling and Analysis Plan* (Warzyn 1992). Specific oversight sample points will be chosen randomly at the time the samples are collected. The oversight samples will be collected from areas that, based on visual observation or historical use of the site, are likely to be contaminated.

Table 4-1 lists the types and quantities of sample containers required for each analysis, proper sample preservation techniques, and holding times.

Sample packaging and shipment will be performed according to EPA requirements as described in Appendix D of the *U.S. EPA Region V Central Regional Laboratory SARA/Superfund Sample Handling Manual* (December 1987). Each sample container will be labeled with the specific sample number, and time and date of collection. Each sample will also be tagged with an EPA sample tag that lists this information, in addition to the type of analysis to be performed on the sample. Each sample will be enclosed in a clear plastic bag and packed with noncombustible, absorbent packing material in a cooler. Coolers will contain enough ice to maintain sample temperatures at $\leq 4^{\circ}\text{C}$. Each cooler will be sealed with two custody seals in such a manner that the seals would be broken if the cooler were opened. Waterproof tape must cover the custody seal. Coolers will be shipped by overnight carrier.

Table 4-1
SAMPLE JAR REQUIREMENTS, PRESERVATIVES, AND HOLDING TIMES

Matrix Type	Analysis	Sample Concentration Level	Bottle Requirements		Temperature Requirements	Preservative Requirements	Holding Times		Minimum Volume	Additional Volume Requirements for MS/MSD Sample	
			No.	Description			Field to Lab	Lab Analysis		No.	Description
Surface Soil/ Sediment	Volatiles, RAS	Low	2	120-mL widemouth glass	Cool to 4° C	NR	24 hrs.	10 days to analysis	240 mL	NR	NR
	Semivolatiles, RAS Pesticides/ PCBs, RAS	Low	1 or 2	8-oz. widemouth jar, or 4-oz. widemouth glass	Cool to 4° C	NR	24 hrs.	10 days to extraction and analyzed within 40 days	6 oz.	NR	NR
	Metals, RAS Cyanide, RAS	Low	1 or 2	8-oz. widemouth glass, or 4-oz. widemouth glass	NR	NR	24 hrs.	6 months; 28 days for Hg; 14 days for cyanide	6 oz.	NR	NR
	TOC, SAS	Low	1	8-oz. widemouth glass	Cool to 4° C	NR	24 hrs.	28 days	4 oz.	NR	NR
	Volatiles, RAS	Low	2	40-ml glass vial	Cool to 4° C	HCl to pH < 2	24 hrs.	7 days to analysis	80 mL	4	40 mL glass vials
Leachate	Semivolatiles, RAS Pesticides/ PCBs, RAS	Low	2 or 3	80-oz. amber glass bottle, or 1-L. amber glass bottle	Cool to 4° C	NR	24 hrs.	10 days to extraction, analyzed within 40 days	1 gallon	2 or 3	80 oz. amber glass bottle, or 1-L. amber glass bottle
	Metals, RAS	Low	1	1-liter polyethylene bottle	NR	HNO ₃ to pH < 2	24 hrs.	6 months; 28 days for Hg	1 liter	NR	NR
	Cyanide, RAS	Low	1	1-liter polyethylene bottle	Cool to 4° C	NaOH to pH > 12	24 hrs.	14 days to analysis	1 liter	NR	NR

Key at end of table.
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Table 4-1 SAMPLE JAR REQUIREMENTS, PRESERVATIVES, AND HOLDING TIMES											
Matrix Type	Analysis	Sample Concentration Level	Bottle Requirements		Temperature Requirements	Preservative Requirements	Holding Times		Minimum Volume	Additional Volume Requirements for MS/MSD Sample	
			No.	Description			Field to Lab	Lab Analysis		No.	Description
Leachate (Cont.)	Chloride ^a , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	28 days to analysis	100 mL	NR	NR
	Sulfate ^a , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	28 days to analysis	50 mL	NR	NR
	Alkalinity ^a , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	14 days to analysis	0.5 liter	NR	NR
	Total hardness, SAS	Low	1	1-liter plastic	Cool to 4° C	HNO ₃ to pH < 2	24 hrs.	6 months to analysis	0.5 liter	NR	NR
	Nitrate-Nitrite Nitrogen, SAS and Nitrite-Nitrogen, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ to pH < 2	24 hrs	28 days to analysis	100 mL	NR	NR
	Ammonia-Nitrogen, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ to pH < 2	24 hrs.	28 days to analysis	400 mL	NR	NR
	TOC, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ or HCl to pH < 2	24 hrs.	28 days to analysis	100 mL	NR	NR
	TDS ^a , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	7 days to analysis	100 mL	NR	NR

Table 4-1 SAMPLE JAR REQUIREMENTS, PRESERVATIVES, AND HOLDING TIMES											
Matrix Type	Analysis	Sample Concentration Level	Bottle Requirements		Temperature Requirements	Preservative Requirements	Holding Times		Minimum Volume	Additional Volume Requirements for MS/MSD Sample	
			No.	Description			Field to Lab	Lab Analysis		No.	Description
Groundwater (monitoring wells)	Volatiles, RAS	Low	2	40-mL glass vial	Cool to 4° C	HCl to pH < 2	24 hrs.	10 days to analysis	80 mL	4	40-mL glass vials
	Semivolatiles, RAS Pesticides/ PCBs, RAS	Low	2 or 3	80-oz. amber glass bottle, or 1-L amber glass bottle	Cool to 4° C	NR	24 hrs.	10 days to extraction, analyzed within 40 days	1 gallon	2 or 3	80-oz. amber glass bottle, or 1-L amber glass bottle
	Metals, RAS	Low	1	1-liter polyethylene bottle	NR	HNO ₃ to pH < 2	24 hrs.	6 months; 28 days for Hg	1 liter	NR	NR
	Cyanide, RAS	Low	1	1-liter polyethylene bottle	Cool to 4° C	NaOH to pH > 12	24 hrs.	14 days to analysis	1 liter	NR	NR
	Alkalinity ^b , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	14 days to analysis	0.5 liter	NR	NR
	Chloride ^b , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	28 days to analysis	100 mL	NR	NR
	Hardness, SAS	Low	1	1-liter plastic	Cool to 4° C	HNO ₃ to pH < 2	24 hrs.	6 months to analysis	0.5 liter	NR	NR
	Sulfate ^b , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	28 days to analysis	50 mL	NR	NR
TOC, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ or HCl to pH < 2	24 hrs.	28 days to analysis	100 mL	NR	NR	

Key at end of table.
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Table 4-1
SAMPLE JAR REQUIREMENTS, PRESERVATIVES, AND HOLDING TIMES

Matrix Type	Analysis	Sample Concentration Level	Bottle Requirements		Temperature Requirements	Preservative Requirements	Holding Times		Minimum Volume	Additional Volume Requirements for MS/MSD Sample	
			No.	Description			Field to Lab	Lab Analysis		No.	Description
Groundwater (monitoring wells) (Cont.)	TDS ^b , SAS	Low	1	1-liter plastic	Cool to 4° C	NR	24 hrs.	7 days to analysis	100 mL	NR	NR
	Nitrate-Nitrite Nitrogen, SAS and Nitrite-Nitrogen, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ to pH <2	24 hrs.	28 days to analysis	200 mL	NR	NR
	Ammonia-Nitrogen, SAS	Low	1	1-liter plastic	Cool to 4° C	H ₂ SO ₄ to pH <2	24 hrs.	28 days to analysis	400 mL	NR	NR
Groundwater (municipal/private wells)	Volatiles, RAS	Low	3	40-mL glass vial	Cool to 4° C	HCl to pH <2	24 hrs.	7 days to analysis	120 mL	6	40-mL vials
	Semivolatiles, RAS Pesticides/ PCBs, RAS	Low	2	1-L amber glass bottle	Cool to 4° C	NR	24 hrs.	10 days to extraction, analyzed within 40 days	2 liters	6	1 L amber glass bottle
	Metals, RAS	Low	1	1-liter polyethylene bottle	Cool to 4° C	HNO ₃ to pH <2	24 hrs.	6 months	500 mL	NR	NR
	Cyanide, RAS	Low	1	1-liter polyethylene bottle	Cool to 4° C	NaOH to pH >12	24 hrs.	14 days to extraction	500 mL	NR	NR
	Mercury	Low	1	1-liter polyethylene bottle	Cool to 4° C	10 ml of Hg preservative ^c	24 hrs.	28 days to analysis	500 mL	NR	NR

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Table 4-1
SAMPLE JAR REQUIREMENTS, PRESERVATIVES, AND HOLDING TIMES

Matrix Type	Analysis	Sample Concentration Level	Bottle Requirements		Temperature Requirements	Preservative Requirements	Holding Times		Minimum Volume	Additional Volume Requirements for MS/MSD Sample	
			No.	Description			Field to Lab	Lab Analysis		No.	Description
Surface water	Volatiles, RAS	Low	2	40-mL glass vial	Cool to 4° C	HCl to pH < 2	24 hrs.	7 days to analysis	80 mL	4	40-mL glass vials
	Semivolatiles, RAS Pesticides/ PCBs, RAS	Low	2 or 3	80-oz. amber glass bottle, or 1-L amber glass bottle	Cool to 4° C	NR	24 hrs.	10 days to extraction, analyzed within 40 days	1 gallon	2 or 3	80 oz. amber glass bottle, or 1-L amber glass bottle
	Metals, RAS	Low	1	1-liter polyethylene bottle	NR	HNO ₃ to pH < 2	24 hrs.	6 months; 28 days for Hg	1 liter	NR	NR
	Cyanide, RAS	Low	1	1-liter polyethylene bottle	Cool to 4° C	NaOH to pH > 12	24 hrs.	14 days to analysis	1 liter	NR	NR

^a May be collected in same bottle.

^b May be collected in same bottle.

^c 10 mL of preservative so that final concentration is 0.05% (w/v) K₂Cr₂O₇ and 0.5% (w/v) HNO₃.

Key:

NR Not required.

TDS Total Dissolved Solids.

TOC Total Organic Carbon.

5. SAMPLE CUSTODY

5.1 INTRODUCTION

EPA Region V policy is to follow the EPA Region V sample custody, or chain-of-custody protocols as described in "NEIC Policies and Procedures," EPA-330/9-78DDI-R, revised June 1985. E & E will maintain final evidence files, including all originals of laboratory reports, under document control in a secure area. A sample or evidence file is under custody if it is:

- in your possession;
- in your view, after being in your possession;
- in your possession and you place it in a secured location; or
- in a designated secure area.

5.2 FIELD-SPECIFIC CUSTODY PROCEDURES

The sample packaging and shipment procedures summarized below and in Appendix C will ensure that the samples will arrive at the laboratory safely and with the chain of custody intact.

5.2.1 Field Procedures

- The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.
- All bottles will be tagged with sample numbers and locations. The SMO number and stickers will be affixed.

- Sample tags are to be completed for each sample using waterproof ink unless this is prohibited by weather conditions. If, due to weather conditions, any writing implement other than a waterproof pen is used, a notation must be made in the field logbook explaining why this occurred.
- The RPM will review all field activities to determine whether proper custody procedures were followed during the fieldwork and decide whether additional samples are required.

5.2.2 Field Logbooks/Documentation

Field logbooks provide the means of recording all field activities performed. As such, entries will be described in as much detail as possible so that persons not present at the time the activities occurred can reconstruct a particular field situation.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the document control center when not in use. Each logbook will be identified by the project-specific document number.

The title page of each logbook will contain the following (at a minimum):

- Person to whom the logbook is assigned;
- Logbook number;
- Project name;
- Project start date; and
- End date.

Logbook entries will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the site, the purpose of their visit, and field sampling or investigation team personnel will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in ink and no erasures will be made. If an incorrect entry is recorded, the information will be crossed out with a single strike mark, dated, and initialed. Whenever a sample is collected or a measurement is made, a detailed description of the location of the station shall be recorded, including approximate compass and distance measurements. The number of the photographs

taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in the Respondent's Sampling and Analysis Plan. The equipment used to collect samples will be noted in the field logbook, along with the time of sampling, sample description, depth at which the sample was collected, and volume and number of containers. Sample identification number will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

The instructions listed above are the minimum requirements for documenting field activities in a field logbook. Additionally, E & E logbook requirements as detailed in *E & E's Standard Operating Procedures For Field Activity Logbooks* (October 1987), shall be followed.

5.2.3 Transfer of Custody and Shipment Procedures

Samples are accompanied by a properly completed chain-of-custody form. The sample numbers and locations will be listed on the chain-of-custody form. When transferring possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to a permanent laboratory, or to/from a secure storage area.

Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be secured with strapping tape and EPA custody seals for shipment to the laboratory. The shipping procedure includes use of a custody seal attached to the front right and back left of the cooler. The custody seals are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.

All shipments will be accompanied by the Chain-of-Custody Record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler for return to the sampling office.

Samples sent by common carrier use a bill of lading. Receipts of bills of lading will be retained as part of the permanent documentation. Commercial carriers are not required to

sign off on the custody form as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

5.3 LABORATORY CUSTODY PROCEDURES

The chain-of-custody procedures for CLP are described in the current organic and inorganic SOW (OLM01 and ILM01, respectively) for Routine Analytical Services (RAS). This same custody procedure applies to SAS analyses. These custody procedures along with the holding time requirements for CLP samples are described in the appropriate SOW documents and SAS requests.

5.4 FINAL EVIDENCE FILES CUSTODY PROCEDURES

The final evidence files from CLP are maintained by the Region V Central Regional Laboratory (CRL) Laboratory Scientific Support Section (LSSS) Data Coordinator. E & E will maintain the project files with all relevant records, reports, logs, field notebooks, photographs, subcontractor reports, and the LSSS data reviews in a secured limited-access area and under the custody of the Site Manager.

6. CALIBRATION PROCEDURES

The consultant's field personnel will perform all required field measurements including pH, conductivity, and temperature. Calibration of the pH instrument will consist of initial calibration with two standard buffer reference solutions bracketing the expected pH of the solution being measured, and pre-measurement and post-measurement verification using these two standards. Field conductivity measurements, if performed, will include daily calibration of the instrument using a standard KCl solution of known conductivity. E & E will document the field calibration and record measurements in the field logbook.

The calibration of laboratory instruments will be consistent with the CLP SOW for organic and inorganic analyses (OLM01 and ILM01, respectively), and with the SAS requests in Appendix B.

7. ANALYTICAL PROCEDURES

Samples will be analyzed for TCL compounds and TAL analytes by the appropriate analytical methods for RAS in the current CLP SOW for organic compound analysis (OLM01) and for inorganic analysis (ILM01). Analytical methods for municipal/private well samples to be analyzed for TCL compounds and TAL analytes are described in the current low concentration SOW for organic compounds (OLC02.0) and the current low concentration SOW for inorganic analytes (ILC02.0). The analytical methods for these samples, which are submitted as SAS requests, as well as the analytical methods for the general chemistry parameters, are specified in the SAS requests (Appendix B). All analytical and QC requirements specified in these documents will be adhered to by the CLP laboratory performing the analyses.

8. DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction will be performed by the CLP laboratories performing the analyses, in accordance with the requirements of the current CLP SOW for organics (OLM01), the current CLP SOW for inorganics (ILM01), and the SAS requests (Appendix B).

Data validation will be performed by EPA Region V CRL LSSS using the Functional Guidelines for the Validation of Organic Data, the Functional Guidelines for Validation of Inorganic Data, the Region V Standard Operating Procedures for Validation of CLP Organic Data, and the guidelines listed in the SAS requests (Appendix B).

Analytical results will be reported in accordance with the current CLP organic and inorganic SOWs (OLM01 and ILM01, respectively) and with the SAS requests (Appendix B).

10. PERFORMANCE AND SYSTEM AUDITS

Project audits can determine adherence to established and documented sample collecting, handling, and documentation procedures. Audits will be performed at the discretion of the RPM and the EPA Region V Quality Assurance Officer (QAO). Results of the audits will be reported to the QAO and the Project Manager, who will identify any areas in which corrective action is needed.

Performance audits of the CLP laboratory are conducted as part of, and according to, the requirements of the CLP Program. Responsibility for these audits rests with EMSL-Las Vegas, Nevada.

11. PREVENTIVE MAINTENANCE

Laboratory equipment will be maintained according to manufacturer's specifications and in such a way that the quality control requirements of CLP will be met for all analyses performed. All laboratories participating in CLP are required under specific SOWs to have standard operating procedures for preventive maintenance of each measurement system and required support activity. All maintenance activity must be documented in logbooks to provide a history of maintenance records.

Preventive maintenance of field equipment will be performed by the consultant, and is discussed in the Respondent's QAPP submitted by the consultant.

12. DATA ASSESSMENT PROCEDURES

All analytical data will be evaluated for precision, accuracy, and completeness. The acceptability of the analytical precision and accuracy will be determined by comparison with the control limits recommended in the current organic and inorganic CLP SOWs (OLM01 and ILM01, respectively) and in the SAS requests. Data determined to be insufficiently precise or inaccurate will be subject to the corrective action prescribed by the appropriate CLP analytical method. The quality control samples used in determination of precision and accuracy have been described in Section 9. Specific equations used to calculate precision, accuracy, and completeness are presented below.

Precision, as measured using replicate analyses, will be expressed in terms of relative percent difference (RPD).

$$RPD = \frac{\text{Concentration 1} - \text{Concentration 2}}{(\text{Concentration 1} + \text{Concentration 2})/2} \times 100$$

Accuracy, as determined from the analysis of an external reference standard will be expressed as percent recovery (% R).

$$\% R = \frac{\text{Measured Concentration}}{\text{Actual Concentration}} \times 100$$

Accuracy, as determined from the analysis of a spiked sample will also be expressed as percent recovery.

$$\% R = \frac{\text{Spiked Sample Concentration} - \text{Sample Concentration}}{\text{Concentration of Spike Added}} \times 100$$

Completeness will describe the number of usable analytical results as a percentage of the total number of samples submitted for analysis.

$$\% \text{ Complete} = \frac{\text{Number of usable results}}{\text{Number of samples submitted}} \times 100$$

13. CORRECTIVE ACTION

Corrective action must be taken any time a situation develops that threatens data quality. Corrective action may be required if field or laboratory audits reveal unacceptable deviations from approved procedures. It may be required any time duplicate or spiked sample analyses exceed the quality control limits or when blank analyses indicate unacceptable levels of contamination. Corrective action may include resampling and reanalysis of a few samples or the cessation of all analyses with subsequent reanalysis of all samples upon resolution of the problem. Specific analytical corrective actions are described in the current CLP organic and inorganic SOWs (OLM01 and ILM01, respectively) and will be adhered to by the laboratory. A quality control problem that cannot be solved by immediate corrective action must be thoroughly investigated to determine the extent of the problem and to ensure that all samples affected by the problem are identified and reanalyzed.

14. QUALITY ASSURANCE REPORTS

Analytical data will be validated in accordance with the following EPA guidance documents:

- *Laboratory Data Validation, Functional Guidelines for Evaluating Organics Analyses*, February 1988.
- *Laboratory Data Validation, Functional Guidelines for Evaluating Inorganic Analyses*, July 1988.
- *Region V Standard Operating Procedure for Validation of CLP Organic Data*, April 1991.

A summary quality assurance statement will accompany the analytical results. This quality assurance report will include an assessment of data quality based on the quality control data as well as an account of any significant quality assurance problems encountered and corrective actions taken. Because data validation of the oversight analyses is their responsibility, EPA Region V CRL will issue the quality assurance assessment of the analytical results to E & E, at the direction of the RPM.

E & E will submit a monthly progress report and biweekly trip reports to EPA. These reports will address any QA issues that arise during the reporting period.

APPENDIX A

TARGET COMPOUND LIST AND

TARGET ANALYTE LIST

TARGET COMPOUND LIST (VOLATILES) AND CONTRACT-REQUIRED QUANTITATION LIMITS* (CROQLs*)

<u>Volatile</u>	<u>CAS Number</u>	<u>Low</u>		<u>Med.</u>
		<u>Water</u>	<u>Soil</u>	<u>Soil</u>
		<u>(ug/L)</u>	<u>(ug/kg)</u>	<u>(ug/kg)</u>
1. Chloromethane	74-87-3	10	10	1,200
2. Bromomethane	74-83-9	10	10	1,200
3. Vinyl chloride	75-01-4	10	10	1,200
4. Chloroethane	75-00-3	10	10	1,200
5. Methylene chloride	75-09-2	10	10	1,200
6. Acetone	67-64-1	10	10	1,200
7. Carbon disulfide	75-15-0	10	10	1,200
8. 1,1-Dichloroethene	75-35-4	10	10	1,200
9. 1,1-Dichloroethane	75-34-3	10	10	1,200
10. 1,2-Dichloroethene(total)	540-59-0	10	10	1,200
11. Chloroform	67-66-3	10	10	1,200
12. 1,2-Dichloroethane	107-06-2	10	10	1,200
13. 2-Butanone	78-93-3	10	10	1,200
14. 1,1,1-Trichloroethane	71-55-6	10	10	1,200
15. Carbon tetrachloride	56-23-5	10	10	1,200
16. Bromodichloromethane	75-27-4	10	10	1,200
17. 1,2-Dichloropropane	78-87-5	10	10	1,200
18. cis-1,3-Dichloropropene	10061-01-5	10	10	1,200
19. Trichloroethene	79-01-6	10	10	1,200
20. Dibromochloromethane	124-48-1	10	10	1,200
21. 1,1,2-Trichloroethane	79-00-5	10	10	1,200
22. Benzene	71-43-2	10	10	1,200
23. trans-1,3-Dichloropropene	10061-02-6	10	10	1,200
24. Bromoform	75-25-2	10	10	1,200
25. 4-Methyl-2-pentanone	108-10-1	10	10	1,200
26. 2-Hexanone	591-78-6	10	10	1,200
27. Tetrachloroethene	127-18-4	10	10	1,200
28. Toluene	108-88-3	10	10	1,200
29. 1,1,2,2-Tetrachloroethane	79-34-5	10	10	1,200
30. Chlorobenzene	108-90-7	10	10	1,200
31. Ethyl benzene	100-41-4	10	10	1,200
32. Styrene	100-42-5	10	10	1,200
33. Xylenes (total)	1330-20-7	10	10	1,200

* Quantitation limits listed for soil/sediment are based on wet weight.
The quantitation limits calculated by the laboratory for soil/sediment,
which are figured on a dry-weight basis, as required by the contract, will be
higher.

TARGET COMPOUND LIST (SEMIVOLATILES) AND CONTRACT-REQUIRED QUANTITATION LIMITS* (CRO)

<u>Semivolatile</u>	<u>CAS Number</u>	<u>Low Water (ug/L)</u>	<u>Med. Soil (ug/kg)</u>	<u>On Soil (ug/kg)</u>
34. Phenol	108-95-2	10	330	10,000
35. bis(2-Chloroethyl) ether	111-44-4	10	330	10,000
36. 2-Chlorophenol	95-57-8	10	330	10,000
37. 1,3-Dichlorobenzene	541-73-1	10	330	10,000
38. 1,4-Dichlorobenzene	106-46-7	10	330	10,000
39. 1,2-Dichlorobenzene	95-50-1	10	330	10,000
40. 2-Methylphenol	95-48-7	10	330	10,000
41. 2,2'-oxybis- (1-Chloropropane)**	108-60-1	10	330	10,000
42. 4-Methylphenol	106-44-5	10	330	10,000
43. N-Nitroso-di-n- dipropylamine	621-64-7	10	330	10,000
44. Hexachloroethane	67-72-1	10	330	10,000
45. Nitrobenzene	98-95-3	10	330	10,000
46. Isophorone	78-59-1	10	330	10,000
47. 2-Nitrophenol	88-75-5	10	330	10,000
48. 2,4-Dimethylphenol	105-67-9	10	330	10,000
49. bis(2-Chloroethoxy) methane	111-91-1	10	330	10,000
50. 2,4-Dichlorophenol	120-83-2	10	330	10,000
51. 1,2,4-Trichlorobenzene	120-82-1	10	330	10,000
52. Naphthalene	91-20-3	10	330	10,000
53. 4-Chloroaniline	106-47-8	10	330	10,000
54. Hexachlorobutadiene	87-68-3	10	330	10,000
55. 4-Chloro-3-methylphenol	59-50-7	10	330	10,000
56. 2-Methylnaphthalene	91-57-6	10	330	10,000
57. Hexachlorocyclopentadiene	77-47-4	10	330	10,000
58. 2,4,6-Trichlorophenol	88-06-2	10	330	10,000
59. 2,4,5-Trichlorophenol	95-95-4	25	1700	50,000
60. 2-Chloronaphthalene	91-58-7	10	330	10,000
61. 2-Nitroaniline	88-74-4	25	1700	50,000
62. Dimethylphthalate	131-11-3	10	330	10,000
63. Acenaphthylene	208-96-8	10	330	10,000

TARGET COMPOUND LIST (SEMIVOLATILES) AND CONTRACT-REQUIRED QUANTITATION LIMITS* (CRLs*)

<u>Semivolatile</u>	<u>CAS Number</u>	<u>Low Water (ug/L)</u>	<u>Med. Soil (ug/kg)</u>	<u>on Soil (ug/kg)</u>
64. 2,6-Dinitrotoluene	606-20-2	10	330	10,000
65. 3-Nitroaniline	99-09-2	25	1700	50,000
66. Acenaphthene	83-32-9	10	330	10,000
67. 2,4-Dinitrophenol	51-28-5	25	1700	50,000
68. 4-Nitrophenol	100-02-7	25	1700	50,000
69. Dibenzofuran	132-64-9	10	330	10,000
70. 2,4-Dinitrotoluene	121-14-2	10	330	10,000
71. Diethylphthalate	84-66-2	10	330	10,000
72. 4-Chlorophenyl-phenyl ether	7005-72-3	10	330	10,000
73. Fluorene	86-73-7	10	330	10,000
74. 4-Nitroaniline	100-01-6	25	1700	50,000
75. 4,6-Dinitro-2-methylphenol	534-52-1	25	1700	50,000
76. N-Nitrosodiphenylamine	86-30-6	10	330	10,000
77. 4-Bromophenyl-phenyl ether	101-55-3	10	330	10,000
78. Hexachlorobenzene	118-74-1	10	330	10,000
79. Pentaqchlorophenol	87-86-5	25	1700	50,000
80. Phenanthrene	85-01-8	10	330	10,000
81. Anthracene	120-12-7	10	330	10,000
82. Carbazole	86-74-8	10	330	10,000
83. Di-n-butylphthalate	86-74-2	10	330	10,000
84. Fluoranthene	206-44-0	10	330	10,000
85. Pyrene	129-00-0	10	330	10,000
86. Butylbenzylphthalate	85-68-7	10	330	10,000
87. 3,3-Dichlorobenzidine	91-94-1	10	330	10,000
88. Benzo(a)anthracene	56-55-3	10	330	10,000
89. Chrysene	210-81-9	10	330	10,000
90. bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10,000
91. Di-n-Octylphthalate	117-84-0	10	330	10,000
92. Benzo(b)fluoranthene	205-99-2	10	330	10,000
93. Benzo(k)fluoranthene	207-08-9	10	330	10,000
94. Benzo(a)pyrene	50-32-8	10	330	10,000
95. Indeno(1,2,3-cd)pyrene	193-39-5	10	330	10,000
96. Dibenzo(a,h)anthracene	53-70-3	10	330	10,000
97. Benzo(g,h,i)perylene	191-24-2	10	330	10,000

* Quantitation limits listed for soil/sediment are based on wet weight.
The quantitation limits calculated by the laboratory for soil/sediment,
based on dry weight as required by the contract, will be higher.

** Previously known by the name of bis(2-chloroisopropyl) ether.

<u>Pesticides/Aroclors</u>	<u>CAS Number</u>	<u>Quantitation Limits</u>	
		<u>Water</u> <u>(ug/L)</u>	<u>Soil**</u> <u>(ug/kg)</u>
98. alpha-BHC	319-84-6	0.05	1.7
99. beta-BHC	319-85-7	0.05	1.7
100. delta-BHC	319-86-8	0.05	1.7
101. gamma-BHC (Lindane)	58-89-9	0.05	1.7
102. Heptachlor	76-44-8	0.05	1.7
103. Aldrin	309-00-2	0.05	1.7
104. Heptachlor epoxide	1024-57-3	0.05	1.7
105. Endosulfan I	959-98-8	0.05	1.7
106. Dieldrin	60-57-1	0.10	3.3
107. 4,4'-DDE	72-55-9	0.10	3.3
108. Endrin	72-20-8	0.10	3.3
109. Endosulfan II	33213-65-9	0.10	3.3
110. 4,4'-DDD	72-54-8	0.10	3.3
111. Endosulfan sulfate	1031-07-8	0.10	3.3
112. 4,4'-DDT	50-29-3	0.10	3.3
113. Methoxychlor	72-43-5	0.50	17.0
114. Endrin ketone	53494-70-5	0.10	3.3
115. Endrin aldehyde	7421-36-3	0.10	3.3
116. alpha-chlordane	5103-71-9	0.05	1.7
117. gamma-chlordane	5103-74-2	0.05	1.7
118. Toxaphene	8001-35-2	5.0	170.0
119. Aroclor-1016	12674-11-2	1.0	33.0
120. Aroclor-1221	11104-28-2	1.0	67.0
121. Aroclor-1232	11141-16-5	2.0	33.0
122. Aroclor-1242	53469-21-9	1.0	33.0
123. Aroclor-1248	12672-29-6	1.0	33.0
124. Aroclor-1254	11097-69-1	1.0	33.0
125. Aroclor-1260	11096-82-5	1.0	33.0

* *There is no differentiation between the preparation of low and medium soil samples in this method for the analysis of pesticides/PCBs.

INORGANIC TARGET ANALYTE LIST

Analyte	Contract-Required ^{1,2}
	Detection Limit (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5,000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5,000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5,000
Selenium	5
Silver	10
Sodium	5,000
Thallium	10
Vanadium	50
Zinc	20
Cyanide	10

- 1 Subject to the restrictions specified in the first page of Part G, Section IV of Exhibit D Inorganic SOW (ILM01.0) (Alternate Methods - Catastrophic Failure), any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract-Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstances:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the values may be reported even though the instrument or method detection limit may not equal the Contract-Required Detection Limit. This is illustrated in the example below:

For lead:

Method in use = ICP

Instrument Detection Limit (IDL) = 40

Sample concentration = 200

Contract-Required Detection Limit (CRDL) = 3

The value of 200 may be reported even though instrument detection limit is greater than CRDL. The instrument or method detection limit must be documented as described in Exhibit E of the Inorganic SOW.

- 2 CRDLs are the instrument detection limits obtained in pure water that must be met using the procedure specified in Exhibit E of the Inorganic SOW. The detection limits for samples may be considerably higher depending on the sample matrix.

CRL'S TARGET COMPOUND LIST SEMIVOLATILES AND QUANTITATION LIMITS (ug/L)

(FOR RESIDENTIAL WELL WATER SAMPLES)

SEMIVOLATILE	CAS NUMBER	QUANTITATION LIMITS
Bis(2-chloroethyl) ether	111-44-4	1.5
Phenol	108-95-2	2.0
2-Chlorophenol	95-57-8	2.0
1,3-Dichlorobenzene	541-73-1	2.0
1,4-Dichlorobenzene	106-46-7	2.0
1,2-Dichlorobenzene	95-50-1	2.5
Benzyl alcohol	100-51-6	2.0
Bis(2-chloroisopropyl) ether	39638-32-9	2.5
2-Methyl phenol	95-48-7	1.0
Hexachloroethane	67-72-1	2.0
N-Nitrosodipropylamine	621-64-7	1.5
Nitrobenzene	98-95-3	2.5
4-Methylphenol	106-44-5	1.0
Isophorone	78-59-1	2.5
2-Nitrophenol	88-75-5	2.0
2,4-Dimethylphenol	105-57-9	2.0
Bis(2-chloroethoxy) methane	111-91-1	2.5
2,4-Dichlorophenol	120-83-2	2.0
1,2,4-Trichlorobenzene	120-82-1	2.0
Naphthalene	91-20-3	2.0
4-Chloroaniline	106-47-8	2.0
Hexachlorobutadiene	87-68-3	2.5
Benzoic Acid	65-85-0	20.0
2-Methyl naphthalene	91-57-6	2.0
4-Chloro-3-methylphenol	59-50-7	1.5
Hexachlorocyclopentadiene	77-47-4	2.0
2,4,6-Trichlorophenol	88-06-2	1.5
2,4,5-Trichlorophenol	95-95-4	1.5
2-Chloro Naphthalene	91-58-7	1.5
Acenaphthylene	208-96-8	1.5
Dimethyl Phthalate	131-11-3	1.5
2,6-Dinitrotoluene	606-20-2	1.0
Acenaphthene	83-32-9	1.5
3-Nitroaniline	99-09-2	2.5
Dibenzofuran	132-64-9	1.0
2,4-Dinitrophenol	51-28-5	(15.0)
2,4-Dinitrotoluene	121-14-2	1.0

CRL'S TARGET COMPOUND LIST SEMIVOLATILES AND QUANTITATION LIMITS (ug/L)

(FOR RESIDENTIAL WELL WATER SAMPLES)

SEMIVOLATILES	CAS NUMBER	QUANTITATION LIMITS
Fluorene	86-73-7	1.0
4-Nitrophenol	100-02-7	1.5
4-Chlorophenyl phenyl ether	7005-72-3	1.0
Diethyl phthalate	84-66-2	1.0
4,5-Dinitro-2-Methylphenol	534-52-1	(15.0)
N-Nitrosodiphenylamine (a)	86-30-6	
Diphenylamine (a)	122-39-4	1.5
4-Nitroaniline	100-01-6	3.0
4-Bromophenyl phenyl ether	101-55-3	1.5
Hexachlorobenzene	118-74-1	1.5
Pentachlorophenol	87-86-5	2.0
Phenanthrene	85-01-8	1.0
Anthracene	120-12-7	2.5
Di-n-butyl phthalate	84-74-2	2.0
Fluoranthene	206-44-0	1.5
Pyrene	129-00-0	1.5
Butyl benzyl phthalate	85-68-7	3.5
Chrysene (b)	218-01-9	
Benzo(a)anthracene (b)	56-55-3	1.5
Bis(2-Ethylhexyl) phthalate	117-81-7	1.0
Di-n-Octyl Phthalate	117-84-0	1.5
Benzo(b)Fluoranthene (c)	205-99-2	
Benzo(k)Fluoranthene (c)	207-08-9	1.5
Benzo(a) Pyrene	50-32-8	2.0
Indeno(1,2,3-cd) Pyrene	193-39-5	3.5
Dibenzo(a,h) Anthracene	53-70-3	2.5
Benzo(g,h,i) Perylene	191-24-2	4.0
2-Nitroaniline	88-74-4	1.0

NOTE: (a) These two compounds are reported as a total.

(b) These two compounds are reported as a total.

(c) These two compounds are reported as a total.

Values in parentheses are estimated.

CRL'S TARGET COMPOUND LIST PESTICIDES/PCBS AND QUANTITATION LIMITS (QLs)

(For Residential Well Water Samples)

Pesticides/PCBs	CAS Number	Quantitation Limits (ug/L)
alpha-BHC	319-84-6	0.010
Beta-BHC	319-85-7	0.005
delta-BHC	319-86-8	0.005
Gamma-BHC (Lindane)	58-89-9	0.005
Heptachlor	76-44-8	0.030
Aldrin	309-00-2	0.005
Heptachlor epoxide	1024-57-3	0.005
Endosulfan I	959-98-8	0.010
Dieldrin	60-57-1	0.010
4,4'-DDE	72-55-9	0.005
Endrin	72-20-8	0.010
Endosulfan II	33213-65-9	0.010
4,4'-DDD	72-54-8	0.020
Endosulfan Sulfate	1031-07-8	0.100
4,4'-DDT	50-29-3	0.020
Methoxychlor	72-43-5	0.020
Endrin Ketone	53494-70-5	0.030
alpha-Chlordane	5103-71-9	0.020
gamma-Chlordane	5103-74-2	0.020
Toxaphene	8001-35-2	0.250
Aroclor-1016	12674-11-2	0.100
Aroclor-1221	11104-28-2	0.100
Aroclor-1232	11141-16-5	0.100
Aroclor-1242	53469-21-9	0.100
Aroclor 1248	12672-29-6	0.100
Aroclor-1254	11097-69-1	0.100
Aroclor-1260	11096-82-5	0.100

CRL'S INORGANIC ANALYTE LIST METALS AND DETECTION LIMITS (DLs)

FOR RESIDENTIAL WELL WATER SAMPLES

<u>Element</u>	<u>Required Detection Limits (ug/L)</u>	<u>Analytical Method</u>
Aluminum (Al)	80	ICP
Antimony (Sb)	2	GFAA
Arsenic (As)	2	GFAA
Barium (Ba)	6	ICP
Beryllium (Be)	1	ICP
Cadmium (Cd)	0.2	GFAA
Calcium (Ca)	500	ICP
Chromium (Cr)	8	ICP
Cobalt (Co)	6	ICP
Copper (Cu)	6	ICP
Iron (Fe)	80	ICP
Lead (Pb)	2	GFAA
Magnesium (Mg)	100	ICP
Manganese (Mn)	5	ICP
Mercury (Hg)	0.1	Cold Vapor AA
Nickel (Ni)	15	ICP
Potassium (K)	5,000	ICP
Selenium (Se)	2	GFAA
Silver (Ag)	6	ICP
Sodium (Na)	1,000	ICP
Thallium (Tl)	2	GFAA
Vanadium (V)	5	ICP
Zinc (Zn)	40	ICP
Cyanide (Cn)	8	AS

APPENDIX B

SPECIAL ANALYTICAL SERVICES REQUESTS

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology and Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: HOD Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

ANALYSIS OF DRINKING WATER/MUNICIPAL/RESIDENTIAL WELL FOR TAL METALS AND CYANIDE WITH LOW QUANTITATION LIMITS

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

One low concentration drinking water sample, one field duplicate, and one field blank for TAL inorganic analysis.

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March-May, 1993

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March-May, 1993 by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

All samples must be analyzed and all results must be submitted within 14 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Perform analysis per Statement of Work (SOW) for low concentration inorganic analysis (ILC01.0).

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

A) Notify the region if dilutions are required.

B) Sample identified as "monitoring well" or "surface water" on the traffic report or on the chain-of-custody, may require dilution. The lab must screen these samples to determine the minimum dilution required. When dilutions are required, the Region must be notified for further instructions regarding reporting. Suspected high concentration samples will be flagged on the traffic report by the sample collector. Report both diluted and undiluted results.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

As per SOW ILC01.0

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz/Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
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As per ILC01.0

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
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As per ILC01.0

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology and Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: HOD Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

ANALYSIS OF DRINKING WATER/MUNICIPAL/RESIDENTIAL WELL FOR TCL ORGANIC COMPOUNDS (VOLATILE, SEMIVOLATILE, AND PESTICIDES/PCBS) WITH LOW QUANTITATION LIMITS

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

One low concentration drinking water sample, one field duplicate, and one field blank for TCL organic analysis.

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March-May,

1993

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March-May, 1993 by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

All samples must be analyzed and all results must be submitted within 14 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Perform analysis per Statement of Work (SOW) for low concentration organic analysis (OLC01.0).

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

A) Notify the region if dilutions are required.

B) Sample identified as "monitoring well" or "surface water" on the traffic report or on the chain-of-custody, may require dilution. The lab must screen these samples to determine the minimum dilution required. When dilutions are required, the Region must be notified for further instructions regarding reporting. Suspected high concentration samples will be flagged on the traffic report by the sample collector. Report both diluted and undiluted results.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

As per SOW OLC01.0

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz/Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
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As per OLC01.0

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
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As per OLC01.0

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

A. EPA Region/Client: Region V / Ecology & Environment, Inc.

B. RSCC Representative: Jan Pels

C. Telephone Number: (312) 353-2720

D. Date of Request: November 18, 1992

E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Determination of Alkalinity (as mg/l CaCO_3) of Water

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 water samples, plus 3 field duplicates and 3 blanks will be collected. One of the 3 samples will be a potentially high concentration leachate sample, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial Action

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May 1993

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May 1993 by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Laboratory must analyze samples within 14 days of sample collection, and report results within 30 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use U.S. EPA Method 310.1 "Alkalinity (Titrametric, pH 4.5)" from *Methods for the Chemical Analysis of Water and Wastes*, 1983 edition, or Methods 403 4c and 4d from *Standard Methods for the Examination of Water and Wastewater*, 16th edition. (Attached)

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- A) Use potentiometric titration to pH 4.5 for alkalinity >20 mg/L as CaCO_3 . For alkalinity <20 mg/L, use EPA Method 310.1 Section 6.2) or *Standard Methods*, Method 403 4d.
- B) Do not titrate volumes >50 mL.
- C) Obtain approval of Region 5 CPMS/CRL prior to use of any other methods.
- D) Use Na_2CO_3 to standardize the titrant. Standardize the pH meter with at least 2 buffers which bracket the end point. Standardize the pH meter and titrant daily.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- A) Report results as mg/l CaCO_3 .
- B) Bench records, tabulating the order of analysis, including the meter calibration, titrant standardization, lab blanks, samples, lab control standards, duplicates, etc. with the resulting titrant volumes or readouts must be provided, along with calculations worksheets.
- C) All records must be clear, legible, and complete enough to recalculate all sample results and QA audits.
- D) Report method of titrant standardization.
- E) QC Reference Samples, or any other standardization material,

will be identified as to source, lot number, etc..
Corresponding "true" or target values and associated 95% confidence levels will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to RAS-CSF)

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312/663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Alkalinity	2 mg/L	±10% or ±2mg/L

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
Lab Blanks	1 per 10 samples	< 2 mg/L
Lab Duplicates	1 per 10 samples	±10% or ±2 mg/L
Lab Control Sample*	1 per set of samples	90-110% Recovery

*(1 set of EPA QC Mineral Reference Samples)

14. Action required if limits are exceeded:

For corrective action and reanalysis, contact the Sample Management Office (SMO).

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
 - 1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
 - 2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
 - 3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
 - 3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
 - 3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
 - 3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
 - 4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ± 2° C.
 - 4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
 - 4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
 - 4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
 - 5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ± 0.2 g (to nearest mg) Na₂CO₃ (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

Approved for NPDES

Issued 1971

Editorial revision 1978

- 5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
 B = ml Na_2CO_3 solution
 C = ml acid used to inflection point

- 5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05 N Na_2CO_3 solution as above.

6. Procedure

6.1 Sample size

- 6.1.1 Use a sufficiently large volume of titrant (> 20 ml in a 50 ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.
 6.1.2 For < 1000 mg CaCO_3 /l use 0.02 N titrant
 6.1.3 For > 1000 mg CaCO_3 /l use 0.1 N titrant
 6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

- 6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask
 6.2.2 Measure pH of sample
 6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.
 6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

- 6.3.1 For alkalinity of < 20 mg/l titrate 100–200 ml as above (6.2) using a 10 ml microburet and 0.02 N acid solution (5.3).
 6.3.2 Stop titration at pH in range of 4.3–4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7. Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/l CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml of sample}}$$

where:

A = ml standard acid

N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l CaCO}_3 = \frac{(2B - C) \times N \times 50,000}{\text{ml of sample}}$$

where:

B = ml titrant to first recorded pH

C = total ml titrant to reach pH 0.3 units lower

N = normality of acid

8. Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

<u>Increment as</u> <u>Alkalinity</u> <u>mg/liter, CaCO₃</u>	<u>Precision as</u> <u>Standard Deviation</u> <u>mg/liter, CaCO₃</u>	<u>Bias,</u> <u>%</u>	<u>Accuracy as</u> <u>Bias,</u> <u>mg/l, CaCO₃</u>
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg CaCO₃/l, the standard deviation was ± 3 .

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

A. EPA Region/Client: Region V / Ecology and Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis for Ammonia-Nitrogen (as mg/l N) in water.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks, will be collected. One of the 3 samples will be a potentially high level leachate sample, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May of 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May of 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples must be analyzed within 28 days of sample collection, and results reported within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use one of the following attached methods:

- a) U.S. EPA Method 350.1 "Nitrogen, Ammonia (Colorimetric, Automated Phenate)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- b) U.S. EPA Method 350.2 "Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric - Distillation Procedure)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- c) U.S. EPA Method 350.3 "Nitrogen, Ammonia (Potentiometric Ion Selective Electrode)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) Store samples at 4°C until analysis and validation of results.
- b) The analytical working range of the shall not exceed 0.01 to 2.0 mg/l.
- c) Check the sample pH (with wide range pH paper). If the pH > 2, contact Region 5 CPMS/CRL for instructions.
- d) Use only the methods specified in Item 7. Obtain approval from CPMS, CRL before using any other method.
- f) The lab must also minimize interferences due to metals, organics, in order to achieve best results.
- j) Use at least 5 calibration standards (including a zero level standard).
- k) Prepare the lab blank using 1 ml/l of H₂SO₄, and analyze like a sample.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Report results as "mg/l Ammonia as N".
- b) Clearly identify the test procedure used.
- c) All bench records, tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, duplicates, etc., with resulting absorbances or concentration readouts, will be provided.
- d) Any sample treatment to remove interferences will be documented.
- e) The lab shall submit photocopies of the instrument readouts (strip charts, printer tapes, etc.)
- f) All records must be clear, legible, and complete enough to recalculate all concentrations.
- g) EPA QC Reference Samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values, along with 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Ammonia (as mg/l N)	0.01 mg/l	± 10% or ± 0.01 mg/l

NOTE: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
Lab Duplicate	1 per 10 samples or at least 1.	$\pm 10\%$ or ± 0.01 mg/l Difference
Lab Blank	1 per 10 samples or at least 1.	< 0.01 mg/l N
Calibration Verification Std.	1 per sample set.	90 - 110% True

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

NITROGEN, AMMONIA

Method 350.1 (Colorimetric, Automated Phenate)

STORET NO. Total 00610

Dissolved 00608

1. Scope and Application
 - 1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.01 to 2.0 mg/l NH_3 as N. This range is for photometric measurements made at 630–660 nm in a 15 mm or 50 mm tubular flow cell. Higher concentrations can be determined by sample dilution. Approximately 20 to 60 samples per hour can be analyzed.
2. Summary of Method
 - 2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.
3. Sample Handling and Preservation
 - 3.1 Preservation by addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Interferences
 - 4.1 Calcium and magnesium ions may be present in concentration sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste. For sea water a sodium potassium tartrate solution is used.
 - 4.2 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.
5. Apparatus
 - 5.1 Technicon AutoAnalyzer Unit (AAI or AAII) consisting of:
 - 5.1.1 Sampler.
 - 5.1.2 Manifold (AAI) or Analytical Cartridge (AAII).
 - 5.1.3 Proportioning pump.
 - 5.1.4 Heating bath with double delay coil (AAI).
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 630–660 nm filters.
 - 5.1.6 Recorder.
 - 5.1.7 Digital printer for AAII (optional).

Approved for NPDES following preliminary distillation, Method 350.2.

Issued 1974

Editorial revision 1978

6. Reagents

- 6.1 Distilled water: Special precaution must be taken to insure that distilled water is free of ammonia. Such water is prepared by passage of distilled water through an ion exchange column comprised of a mixture of both strongly acidic cation and strongly basic anion exchange resins. The regeneration of the ion exchange column should be carried out according to the instruction of the manufacturer.

NOTE 1: All solutions must be made using ammonia-free water.

- 6.2 Sulfuric acid 5N: Air scrubber solution. Carefully add 139 ml of conc. sulfuric acid to approximately 500 ml of ammonia-free distilled water. Cool to room temperature and dilute to 1 liter with ammonia-free distilled water.
- 6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, dissolve 83 g phenol in 500 ml of distilled water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with distilled water.
- 6.4 Sodium hypochlorite solution: Dilute 250 ml of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 ml with distilled water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.
- 6.5 Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA (disodium salt) and approximately six pellets of NaOH in 1 liter of distilled water.
- NOTE 2:** On salt water samples where EDTA solution does not prevent precipitation of cations, sodium potassium tartrate solution may be used to advantage. It is prepared as follows:
- 6.5.1 Sodium potassium tartrate solution: 10% $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. To 900 ml of distilled water add 100 g sodium potassium tartrate. Add 2 pellets of NaOH and a few boiling chips, boil gently for 45 minutes. Cover, cool, and dilute to 1 liter with ammonia-free distilled water. Adjust pH to 5.2 ± 0.05 with H_2SO_4 . After allowing to settle overnight in a cool place, filter to remove precipitate. Then add 1/2 ml Brij-35⁽⁴⁾ (available from Technicon Corporation) solution and store in stoppered bottle.
- 6.6 Sodium nitroprusside (0.05%): Dissolve 0.5 g of sodium nitroprusside in 1 liter of distilled water.
- 6.7 Stock solution: Dissolve 3.819 g of anhydrous ammonium chloride, NH_4Cl , dried at 105°C , in distilled water, and dilute to 1000 ml. 1.0 ml = 1.0 mg $\text{NH}_3\text{-N}$.
- 6.8 Standard Solution A: Dilute 10.0 ml of stock solution (6.7) to 1000 ml with distilled water. 1.0 ml = 0.01 mg $\text{NH}_3\text{-N}$.
- 6.9 Standard solution B: Dilute 10.0 ml of standard solution A (6.8) to 100.0 ml with distilled water. 1.0 ml = 0.001 mg $\text{NH}_3\text{-N}$.

- 6.10 Using standard solutions A and B, prepare the following standards in 100 ml volumetric flasks (prepare fresh daily):

<u>NH₃-N, mg/l</u>	<u>ml Standard Solution/100 ml</u>
	<u>Solution B</u>
0.01	1.0
0.02	2.0
0.05	5.0
0.10	10.0
	<u>Solution A</u>
0.20	2.0
0.50	5.0
0.80	8.0
1.00	10.0
1.50	15.0
2.00	20.0

NOTE 3: When saline water samples are analyzed, Substitute Ocean Water (SOW) should be used for preparing the above standards used for the calibration curve; otherwise, distilled water is used. If SOW is used, subtract its blank background response from the standards before preparing the standard curve.

Substitute Ocean Water (SOW)

NaCl	24.53 g/l	NaHCO ₃	0.20 g/l
MgCl ₂	5.20 g/l	KBr	0.10 g/l
Na ₂ SO ₄	4.09 g/l	H ₃ BO ₃	0.03 g/l
CaCl ₂	1.16 g/l	SrCl ₂	0.03 g/l
KCl	0.70 g/l	NaF	0.003 g/l

7. Procedure

- 7.1 Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples. For example, if the samples have been preserved with 2 ml conc. H₂SO₄/liter, the wash water and standards should also contain 2 ml conc. H₂SO₄/liter.
- 7.2 For a working range of 0.01 to 2.00 mg NH₃-N/l (AAI), set up the manifold as shown in Figure 1. For a working range of .01 to 1.0 mg NH₃-N/l (AAII), set up the manifold as shown in Figure 2. Higher concentrations may be accommodated by sample dilution.
- 7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through sample line.
- 7.4 For the AAI system, sample at a rate of 20/hr, 1:1. For the AAII use a 60/hr 6:1 cam with a common wash.

- 7.5 Arrange ammonia standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.
- 7.6 Switch sample line from distilled water to sampler and begin analysis.
8. Calculations
 - 8.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.
9. Precision and Accuracy
 - 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43 mg $\text{NH}_3\text{-N/l}$, the standard deviation was ± 0.005 .
 - 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.16 and 1.44 mg $\text{NH}_3\text{-N/l}$, recoveries were 107% and 99%, respectively.

Bibliography

1. Hiller, A., and Van Slyke, D., "Determination of Ammonia in Blood", J. Biol. Chem. 102, p 499 (1933).
2. O'Connor, B., Dobbs, R., Villiers, B., and Dean, R., "Laboratory Distillation of Municipal Waste Effluents", JWPCF 39, R 25 (1967).
3. Fiore, J., and O'Brien, J. E., "Ammonia Determination by Automatic Analysis", Wastes Engineering 33, p 352 (1962).
4. A wetting agent recommended and supplied by the Technicon Corporation for use in AutoAnalyzers.
5. ASTM "Manual on Industrial Water and Industrial Waste Water", 2nd Ed., 1966 printing, p 418.
6. Booth, R. L., and Lobring, L. B., "Evaluation of the AutoAnalyzer II: A Progress Report" in Advances in Automated Analysis: 1972 Technicon International Congress, Vol. 8, p 7-10, Mediad Incorporated, Tarrytown, N.Y., (1973).
7. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 616, Method 604 (1975).

350.1-5

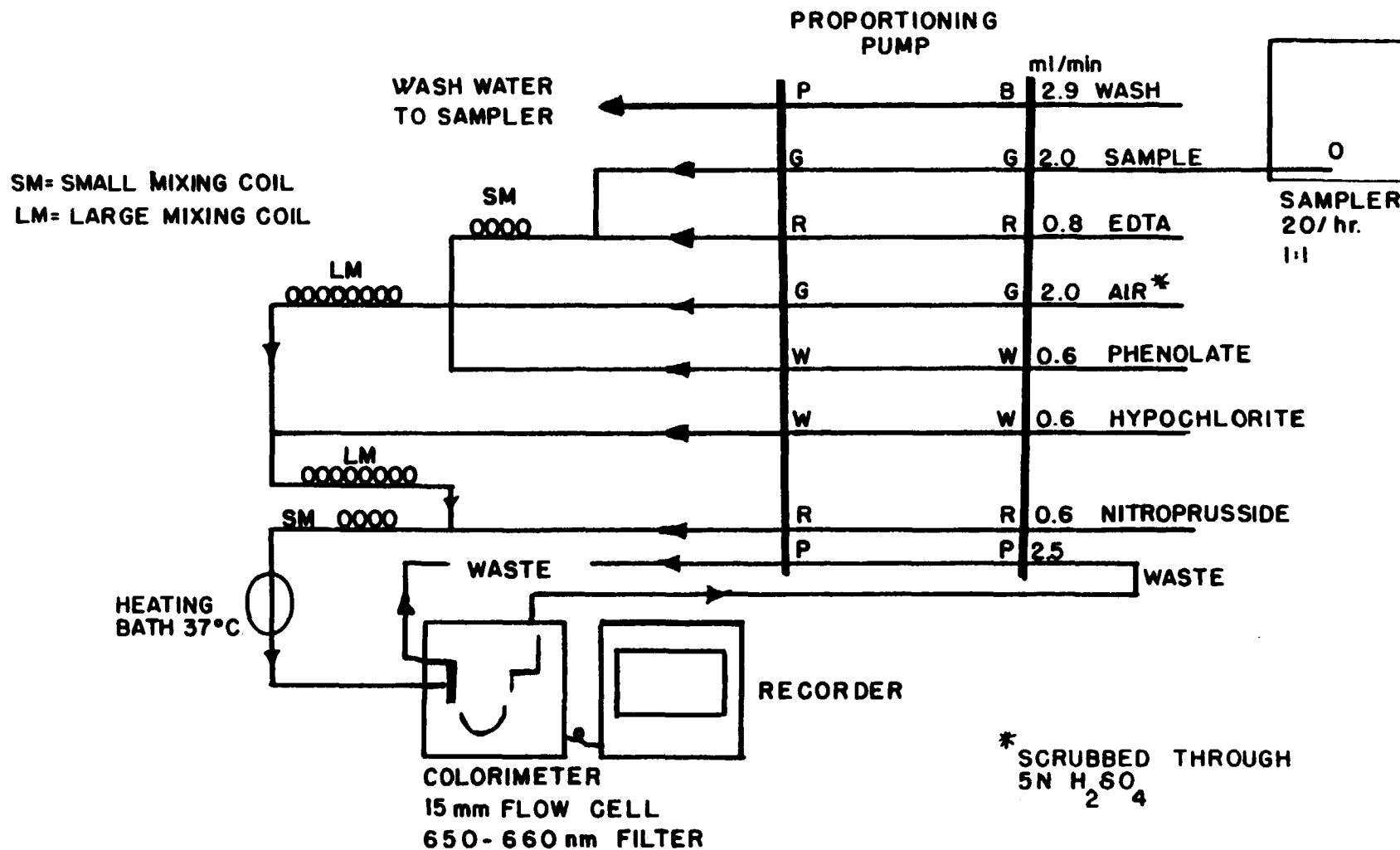


FIGURE 1 AMMONIA MANIFOLD AA I

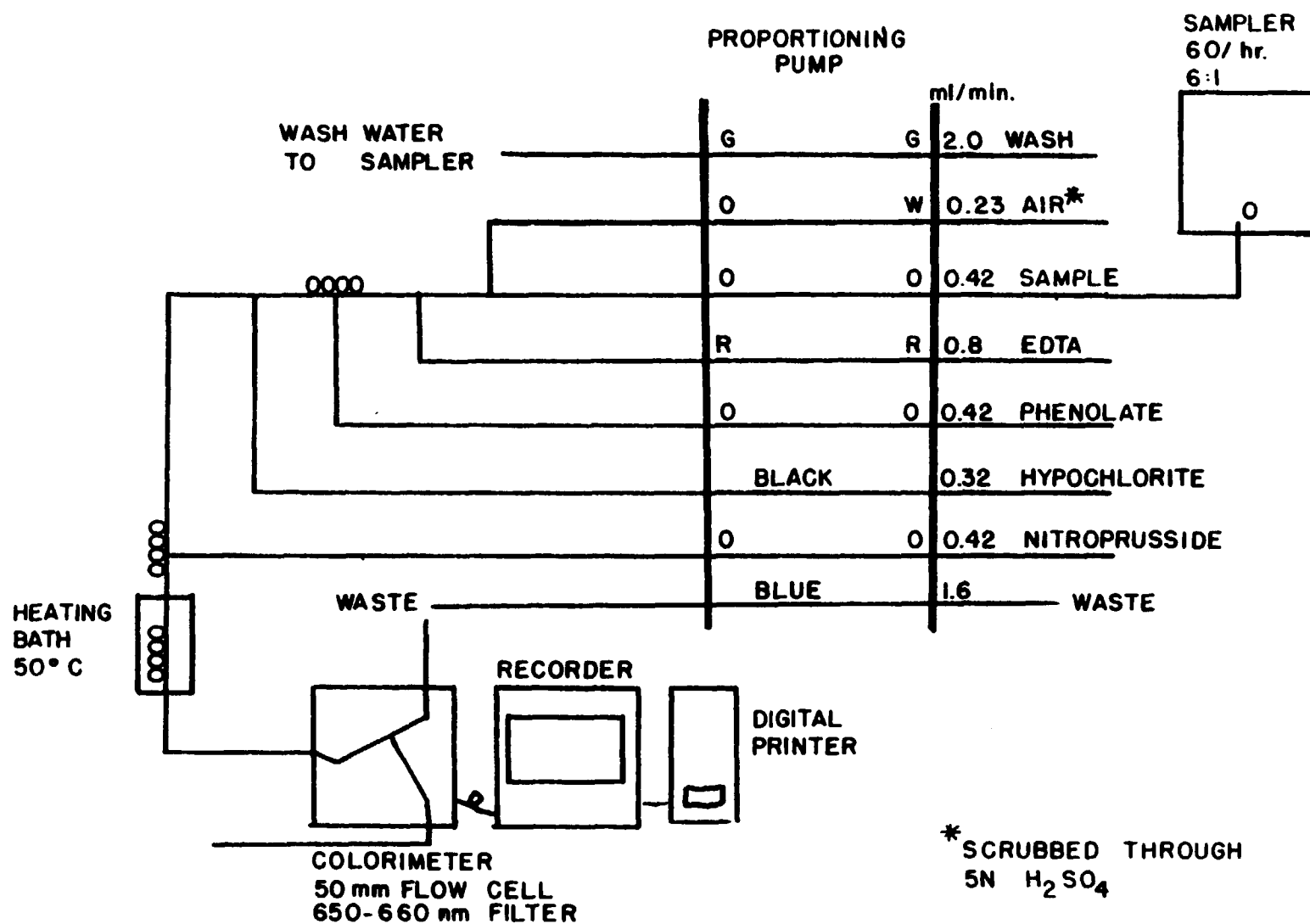


FIGURE 2. AMMONIA MANIFOLD AA II

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
 - 1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
 - 1.2 The method covers the range from about 0.05 to 1.0 mg $\text{NH}_3\text{-N/l}$ for the colorimetric procedure, from 1.0 to 25 mg/l for the titrimetric procedure, and from 0.05 to 1400 mg/l for the electrode method.
 - 1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
 - 2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
 - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
 - 4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
 - 4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
 - 4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

Approved for NPDES
Issued 1971
Editorial revision 1974

5. Apparatus
- 5.1 An all-glass distilling apparatus with an 800–1000 ml flask.
 - 5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.
 - 5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm \pm 1.5 mm inside measurement from bottom.
 - 5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.
6. Reagents
- 6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
NOTE 1: All solutions must be made with ammonia-free water.
 - 6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg $\text{NH}_3\text{-N}$. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.
 - 6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.
 - 6.4 Boric acid solution (20 g/l): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.
 - 6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.
NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.
 - 6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.
NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).
 - 6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $\text{Na}_2\text{B}_4\text{O}_7$, or 9.5 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ per liter) and dilute to 1 liter.
 - 6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg $\text{NH}_3\text{-N}$). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2 -free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2 -free distilled water.
NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

- 6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3 , oven-dried at 140°C , and diluting to 1000 ml with CO_2 -free distilled water.
- 6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.
- 6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:
- Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.
 - Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.
7. Procedure
- 7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.
- 7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.
- 7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.
- NOTE 5:** The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.
- Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.
- 7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.
- 7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 , matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

<u>ml of Standard</u> <u>1.0 ml = 0.01 mg NH₃-N</u>	<u>mg NH₃-N/50.0 ml</u>
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH₃-N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 0.28 \times 1,000}{S}$$

where:

A = ml 0.02 N H₂SO₄ used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l NH}_3 - \text{N} = \frac{A \times 1,000}{D} \times \frac{B}{C}$$

where:

A = mg NH₃-N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$\text{mg/l NH}_3 - \text{N} = \frac{500}{D} \times A$$

where:

A = mg NH₃-N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426-74, Method A, p 237 (1976).

NITROGEN, AMMONIA

Method 350.3 (Potentiometric, Ion Selective Electrode)

STORET NO. Total 00610

Dissolved 00608

1. Scope and Application
 - 1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
 - 1.2 This method covers the range from 0.03 to 1400 mg $\text{NH}_3\text{-N/l}$. Color and turbidity have no effect on the measurements, thus, distillation may not be necessary.
2. Summary of Method
 - 2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.
 - 2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.
3. Sample Handling and Preservation
 - 3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C .
4. Interferences
 - 4.1 Volatile amines act as a positive interference.
 - 4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.
5. Apparatus
 - 5.1 Electrometer (pH meter) with expanded mV scale or a specific ion meter.
 - 5.2 Ammonia selective electrode, such as Orion Model 95-10 or EIL Model 8002-2.
 - 5.3 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
6. Reagents
 - 6.1 Distilled water: Special precautions must be taken to insure that the distilled water is free of ammonia. This is accomplished by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
 - 6.2 Sodium hydroxide, 10N: Dissolve 400 g of sodium hydroxide in 800 ml of distilled water. Cool and dilute to 1 liter with distilled water (6.1).
 - 6.3 Ammonium chloride, stock solution: $1.0 \text{ ml} = 1.0 \text{ mg } \text{NH}_3\text{-N}$. Dissolve 3.819 g NH_4Cl in water and bring to volume in a 1 liter volumetric flask using distilled water (6.1).

Issued 1974

Approved for NPDES following preliminary distillation (Method 350.2)

- 6.4 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg $\text{NH}_3\text{-N}$. Dilute 10.0 ml of the stock solution (6.3) to 1 liter with distilled water (6.1) in a volumetric flask.
- NOTE 1:** When analyzing saline waters, standards must be made up in synthetic ocean water (SOW); found in Nitrogen, Ammonia: Colorimetric, Automated Phenate Method (350.1).
7. Procedure
- 7.1 Preparation of standards: Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium chloride.
- 7.2 Calibration of electrometer: Place 100 ml of each standard solution in clean 150 ml beakers. Immerse electrode into standard of lowest concentration and add 1 ml of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.
- NOTE 2:** The pH of the solution after the addition of NaOH must be above 11.
- Caution:** Sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.
- 7.3 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Using semilogarithmic graph paper, plot the concentration of ammonia in mg $\text{NH}_3\text{-N/l}$ on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.
- 7.4 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.
- 7.5 Sample measurement: Follow the procedure in (7.2) for 100 ml of sample in 150 ml beakers. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve. If a specific ion meter is used, read the ammonia level directly in mg $\text{NH}_3\text{-N/l}$.
8. Precision and Accuracy
- 8.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg $\text{NH}_3\text{-N/l}$, standard deviations were ± 0.038 , ± 0.017 , ± 0.007 , and ± 0.003 , respectively.
- 8.2 In a single laboratory (EMSL), using surface water samples at concentrations of 0.19 and 0.13 mg $\text{NH}_3\text{-N/l}$, recoveries were 96% and 91%, respectively.

Bibliography

1. Booth, R. L., and Thomas, R. F., "Selective Electrode Determination of Ammonia in Water and Wastes", *Envir. Sci. Technology*, 7, p 523-526 (1973).
2. Banwart, W. L., Bremner, J. M., and Tabatabai, M. A., "Determination of Ammonium in Soil Extracts and Water Samples by an Ammonia Electrode", *Comm. Soil Sci. Plant.*, 3, p 449 (1952).
3. Midgley, D., and Torrance, K., "The Determination of Ammonia in Condensed Steam and Boiler Feed-Water with a Potentiometric Ammonia Probe", *Analyst*, 97 p 626-633 (1972).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

A. EPA Region/Client: Region V / Ecology and Environment, Inc.

B. RSCC Representative: Jan Pels

C. Telephone Number: 312-353-2720

D. Date of Request: November 18, 1992

E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis for Total Chloride (as mg/l Cl) in Water.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks, will be collected. One of three 3 samples will be a potentially high level leachate sample, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May of 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May of 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples must be analyzed within 28 days of sample collection, and results reported within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use one of the following attached methods:

- a) U.S. EPA Method 325.1 "Chloride, (Colorimetric, Automated, Ferricyanide AAI), from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- b) U.S. EPA Method 325.2 "Chloride, (Colorimetric, Automated, Ferricyanide, AA II)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- c) U.S. EPA Method 325.3 "Chloride (Titrimetric, Mercuric Nitrate)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) The calibration range for this analysis shall not exceed 1 - 400 mg/l. Any samples with concentrations of > 400 mg/l must be diluted and reanalyzed.
- b) For samples with concentrations of < 200 mg/l, use Method 325.1 or 325.2 to quantify any results.
- c) For samples with concentrations of 200 - 400 mg/l, Method 325.3 must be used to quantify any results.
- d) Use only the methods specified in Item 7. Obtain approval from Region 5 CPMS/CRL before using any other method.
- e) The lab must also minimize interferences due to metals and organics, to achieve best results.
- f) Use at least 5 calibration standards (including a zero level standard).

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Report results as "Chloride as mg/l Cl".
- b) Clearly identify the test procedure used.

- c) All bench records, tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, duplicates, etc., with resulting absorbances or concentration readouts, will be provided.
- d) Any sample treatment to remove interferences will be documented.
- e) The lab shall submit photocopies of the instrument readouts (strip charts, printer tapes, etc.)
- f) All records must be clear, legible, and complete enough to recalculate all concentrations.
- g) Any EPA QC Reference Samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values, along with 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Chloride	1.0 mg/l	± 10% or ± 1.0 mg/l

NOTE: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
Lab Duplicate	1 per 10 samples, or at least 1	$\pm 10\%$ or ± 1.0 mg/l Difference
Lab Blank	1 per 10 samples, or at least 1	< 1.0 mg/l
Calibration Verification Std.	1 per sample set.	90 - 110% True

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

CHLORIDE

Method 325.1 (Colorimetric, Automated Ferricyanide AAD)

STORET NO. 00940

1. Scope and Application
 - 1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 250 mg Cl/l. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
 - 2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
 - 3.1 No special requirements.
4. Interferences
 - 4.1 No significant interferences.
5. Apparatus
 - 5.1 Technicon AutoAnalyzer consisting of:
 - 5.1.1 Sampler I.
 - 5.1.2 Continuous filter.
 - 5.1.3 Manifold.
 - 5.1.4 Proportioning pump.
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
 - 5.1.6 Recorder.
6. Reagents
 - 6.1 Ferric Ammonium Sulfate: Dissolve 60 g of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in approximately 500 ml distilled water. Add 355 ml of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.
 - 6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of $\text{Hg}(\text{SCN})_2$ in 1 liter of distilled water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.
 - 6.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.
 - 6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

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Issued 1971

<u>ml of Stock Solution</u>	<u>Conc., mg/l</u>
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0
50.0	250.0

7. Procedure

- 7.1 No advance sample preparation is required. Set up manifold as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one distilled water intake line.
- 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.
- 7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.
- 7.4 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.
- 7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1, 100, and 250 mg Cl/l, the standard deviation was ± 0.3 .
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 10 and 100 mg Cl/l, recoveries were 97% and 104%, respectively.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Waste Engr., 33, 670-672 (Dec. 1962).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 613, Method 602 (1975).

325.1-3

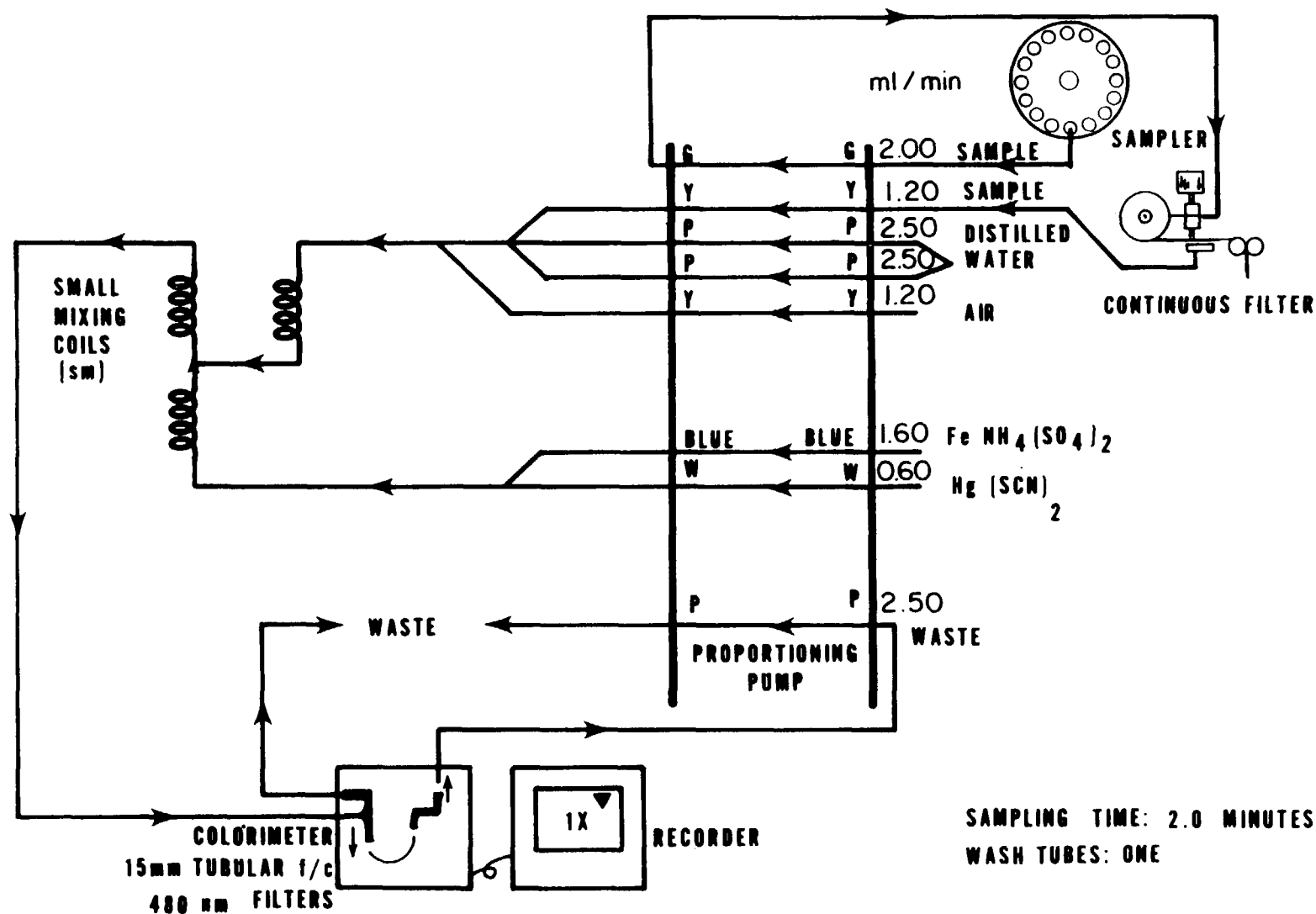


FIGURE 1. CHLORIDE MANIFOLD AA-I

CHLORIDE

Method 325.2 (Colorimetric, Automated Ferricyanide AAI)

STORET NO. 00940

1. Scope and Application
 - 1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 200 mg Cl/l. This range may be extended by sample dilution. Approximately 30 samples per hour can be analyzed.
2. Summary of Method
 - 2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
 - 3.1 No special requirements.
4. Interferences
 - 4.1 No significant interferences.
5. Apparatus
 - 5.1 Technicon AutoAnalyzer consisting of:
 - 5.1.1 Sampler.
 - 5.1.2 Continuous filter (optional).
 - 5.1.3 Analytical cartridge.
 - 5.1.4 Proportioning pump.
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
 - 5.1.6 Recorder.
 - 5.1.7 Digital printer (optional).
6. Reagents
 - 6.1 Mercuric thiocyanate solution: Dissolve 4.17 gm of Hg(SCN)_2 in 500 ml of methanol. Dilute to 1 liter with methanol, mix and filter through filter paper.
 - 6.2 Ferric nitrate solution, 20.2%: Dissolve 202 gm of $\text{Fe(NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in 500 ml of distilled water. Add 31.5 ml conc nitric acid, mix and dilute to 1 liter with distilled water.
 - 6.3 Color reagent: Add 150 ml of mercuric thiocyanate solution (6.1) to 150 ml of ferric nitrate solution (6.2), mix, and dilute to 1 liter with distilled water.
 - 6.4 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.
 - 6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

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Issued 1978

<u>ml of Stock Solution</u>	<u>Conc., mg/l</u>
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

7. Procedure

- 7.1 Where particulate matter is present, the sample must be filtered prior to the determination. This can be accomplished by having the Technicon continuous filter as an integral part of the system. The sample may be centrifuged in place of filtration.
- 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.
- 7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.
- 7.4 When a stable baseline has been obtained, start the sampler.

8. Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

- 9.1 Precision and accuracy data are not available at this time.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Waste Engr., 33, 670-672 (Dec. 1962).
2. Technicon AutoAnalyzer II, Industrial Method No. 99-70W, Technicon Industrial Systems, Tarrytown, N. Y., 10591 (Sept. 1973).

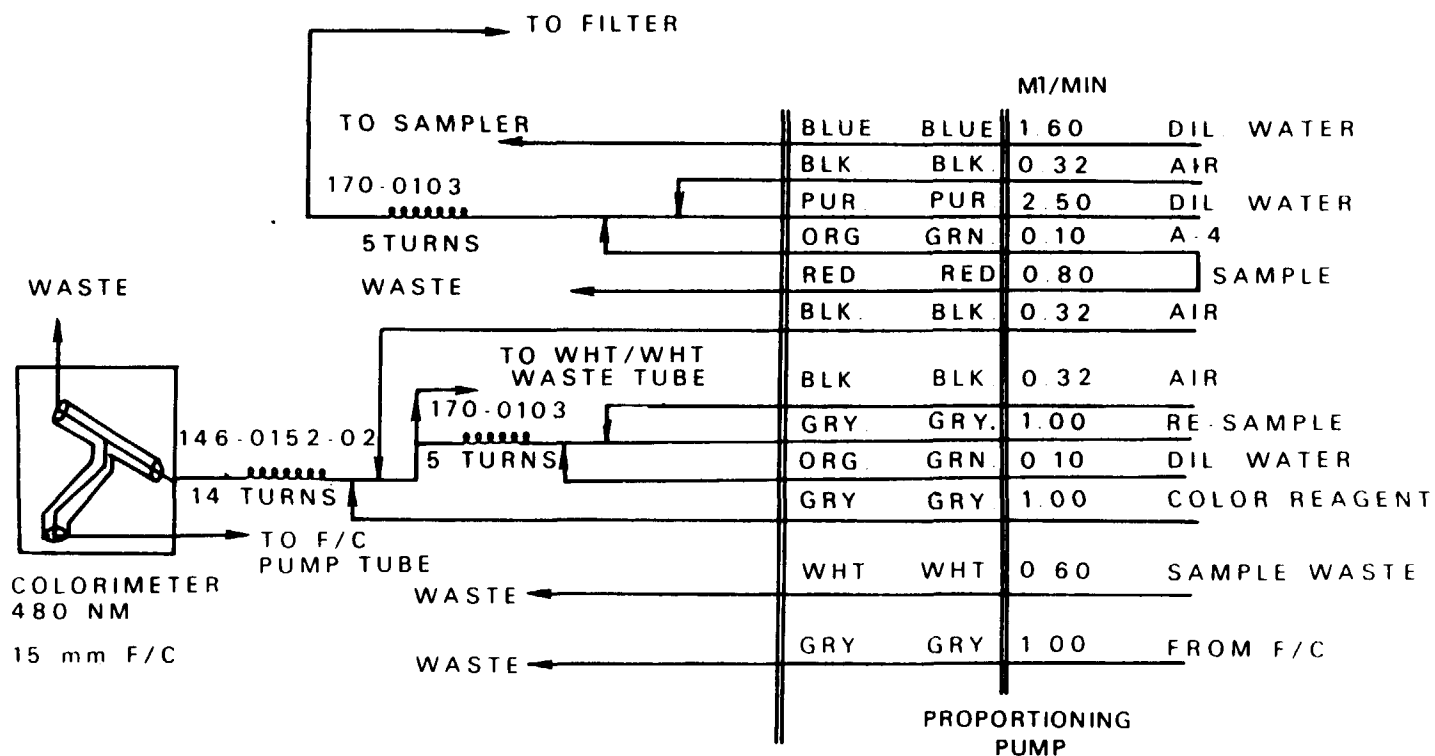


FIGURE 1
CHLORIDE MANIFOLD AA 11

CHLORIDE

Method 325.3 (Titrimetric, Mercuric Nitrate)

STORET NO. 00940

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.
 - 1.3 Automated titration may be used.
2. Summary of Method
 - 2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
3. Comments
 - 3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
 - 3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H_2O_2 .
4. Apparatus
 - 4.1 Standard laboratory titrimetric equipment including a 1 ml or 5 ml microburet with 0.01 ml graduations.
5. Reagents
 - 5.1 Standard sodium chloride, 0.025 N: Dissolve $1.4613 \text{ g} \pm 0.0002 \text{ g}$ sodium chloride (dried at 600°C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark $1 \text{ ml} = 886.5 \mu\text{g Cl}$.
 - 5.2 Nitric acid, HNO_3 solution (3 + 997)
 - 5.3 Sodium hydroxide solution, NaOH , (10 g/1)
 - 5.4 Hydrogen peroxide (30%), H_2O_2
 - 5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric and dilute to the mark.
 - 5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 900 ml of distilled water acidified with 5.0 ml conc. HNO_3 in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.
 - 5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 50 ml of distilled water acidified with 0.5 ml conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard

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Issued 1971

Editorial revision 1978 and 1982

sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.025 N and check. Store in a dark bottle.

- 5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 25 ml of distilled water acidified with 0.25 ml of conc. HNO_3 (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 μg of chloride.
- 5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100 ml volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.
- 5.10 Xylene cyanole FF solution: Dissolve 0.005 g of xylene cyanole FF dye in 95% ethanol or isopropanol in a 100 ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

6. Procedure

- 6.1 Use 50 ml of sample or an aliquot of sample diluted to 50 ml with distilled water, so that the concentration of chloride does not exceed 20 mg/aliquot. If the sample or aliquot contains more than 2.5 mg of chloride, use 0.025N mercuric nitrate titrant (5.7) in step 6.6. If the sample or aliquot contains less than 2.5 mg of chloride, use 0.0141N mercuric nitrate titrant (5.8) in step 6.6. Determine an indicator blank on 50 ml chloride-free water using step 6.6. If the sample contains less than 0.1 mg/l of chloride concentrate an appropriate volume to 50 ml.
- 6.2 Add 5 drops of mixed indicator reagent (5.9), shake or swirl solution.
- 6.3 If a blue-violet or red color appears add HNO_3 solution (5.2) dropwise until the color changes to yellow.
- 6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO_3 solution (5.2) dropwise until the color changes to yellow.
- 6.5 Add 1 ml excess HNO_3 solution (5.2).
- 6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Xylene cyanole FF solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.
- 6.7 Additional steps to eliminate particular interferences:
 - 6.7.1 If chromate is present and iron is not present the end point may be difficult to detect.
be an olive-purple color.
 - 6.7.2 If chromate is present at $> 100 \text{ mg/l}$ and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).
 - 6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).
 - 6.7.4 If sulfite ion is present, add 0.5 ml of H_2O_2 solution (5.4) to 50 ml sample and mix for 1 minute.

7. Calculation

$$\text{mg chloride/l} = \frac{(A - B)N \times 35,450}{\text{ml of sample}}$$

where:

A = ml titrant for sample

B = ml titrant for blank

N = normality mercuric nitrate titrant

$$\text{mg NaCl/l} = \text{mg chloride/l} \times 1.65$$

8. Precision and Accuracy

8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

<u>Increment as Chloride mg/liter</u>	<u>Precision as Standard Deviation mg/liter</u>	<u>Bias, %</u>	<u>Accuracy as Bias, mg/liter</u>
17	1.54	+2.16	+0.4
18	1.32	+3.50	+0.6
91	2.92	+0.11	+0.1
97	3.16	-0.51	-0.5
382	11.70	-0.61	-2.3
398	11.80	-1.19	-4.7

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/l, the standard deviation was ± 1.0 .

8.3 A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate and 42.5 mg/l total alkalinity (contributed by NaHCO_3) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D512-67, Method A, p 270 (1976).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology & Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: (312) 353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Determination of Total Hardness (as mg/l CaCO₃) of Water.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks. One of the 3 samples will be a potentially high level leachate sample, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

SUPERFUND - Remedial Action.

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May,

1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Laboratory must analyze samples and report results within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use the following attached EPA methods:

- a) U.S. EPA Method 130.1, "Hardness, Total (mg/l as CaCO_3), (Colorimetric, Automated EDTA), from Methods for the Chemical Analysis of Water and Wastes, 1983 edition.
- b) U.S. EPA Method 130.2 "Hardness, Total (mg/L as CaCO_3) (Titrametric, EDTA) from *Methods for the Chemical Analysis of Water and Wastes*, 1983 edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) For normal to high-hardness (> 5 mg/L), use 25 ml of sample, 1 - 2 ml buffer solution, 1-2 drops indicator solution.
- b) For low hardness (< 5 mg/L) use larger, 100ml sample, and proportionately larger amounts (4 - 5X) of buffer and indicator.
- c) Use one of the listed inhibitors only if necessary.
- d) Standardize the EDTA titrant with standard calcium solution (Sec. 6.4.5) on a daily basis.
- e) Obtain approval of CPMS, CRL prior to use of any other methods.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Report results as mg/L CaCO_3 .
- b) Bench records, tabulating the order of analysis, including the titrant standardization, lab blanks, samples, lab control standards, duplicates, etc. with the resulting titrant volumes or readouts, must be provided, along with calculation

worksheets.

- c) All records must be clear, legible, and complete enough to re calculate all sample results and QA audits.
- d) Report method of titrant standardization
- e) QC Reference Samples, or any other standardization material, will be identified as to source, lot number, etc.. Corresponding "true" or target values and associated 95% confidence levels will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - 312/663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Total Hardness	1 mg/l	±10% or ±1mg/l

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
Lab Blanks	1 per 10 samples	< 1 mg/l
Lab Duplicates	1 per 10 samples	±10% or ±1 mg/l
Calcium Standard	1 per sample set	85-115% Recovery

14. Action required if limits are exceeded:

corrective action and re analysis, contact the Sample Management Office (SMO).

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

HARDNESS, Total (mg/1 as CaCO₃)

Method 130.1 (Colorimetric, Automated EDTA)

STORET NO. 00900

1. Scope and Application

1.1 This automated method is applicable to drinking, surface, and saline waters. The applicable range is 10 to 400 mg/1 as CaCO₃. Approximately 12 samples per hour can be analyzed.

2. Summary of Method

2.1 The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.

3. Sample Handling and Preservation

3.1 Cool to 4°C, HNO₃ to pH < 2.

4. Interferences

4.1 No significant interferences.

5. Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous Filter.

5.1.3 Manifold.

5.1.4 Proportioning Pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.

5.1.6 Recorder equipped with range expander.

6. Reagents

6.1 Buffer: Dissolve 67.6 g NH₄Cl in 572 ml of NH₄OH and dilute to 1 liter with distilled water.

6.2 Calmagite Indicator: Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.

6.3 Monomagnesium ethylenediamine-tetraacetate (MgEDTA): Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.

6.4 Stock Solution: Weigh 1.000 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all CaCO₃ has dissolved. Add 200 ml of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH₄OH and dilute to 1000 ml with distilled water. 1 ml = 1.0 mg CaCO₃.

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6.4.1 Dilute each of the following volumes of stock solutions to 250 ml in a volumetric flask for appropriate standards:

<u>Stock Solution, ml</u>	<u>CaCO₃, mg/l</u>
2.5	10.0
5.0	20.0
10.0	40.0
15.0	60.0
25.0	100.0
35.0	140.0
50.0	200.0
75.0	300.0
100.0	400.0

6.5 Ammonium Hydroxide, 1N: Dilute 70 ml of conc. NH₄OH to 1 liter with distilled water.

7. Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Neutralize 50.0 ml of sample with 1N ammonium hydroxide (6.5) and note volume of NH₄OH used.

7.3 Set up manifold as shown in Figure 1.

7.4 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

7.5 Place distilled water wash tubes in alternate openings in Sampler and set sample timing at 2.5 minutes.

7.6 Arrange working standards in Sampler in order of decreasing concentrations. Complete loading of Sampler tray with unknown samples.

7.7 Switch sample line from distilled water to Sampler and begin analysis.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of processed standards against concentration values. Compute concentration of samples by comparing sample peak heights with standard curve. Correct for amount of NH₄OH used in 7.2 as follows:

$$\text{mg/l} = \frac{A}{50} \times B$$

where:

A = Vol. of sample plus volume of NH₄OH

B = Concentration from standard curve

9. Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 19, 120, 385, and 366 mg/l as CaCO_3 , the standard deviations were ± 1.5 , ± 1.5 , ± 4.5 , and ± 5.0 , respectively.
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 39 and 296 mg/l as CaCO_3 , recoveries were 89% and 93%, respectively.

Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).

130.1-4

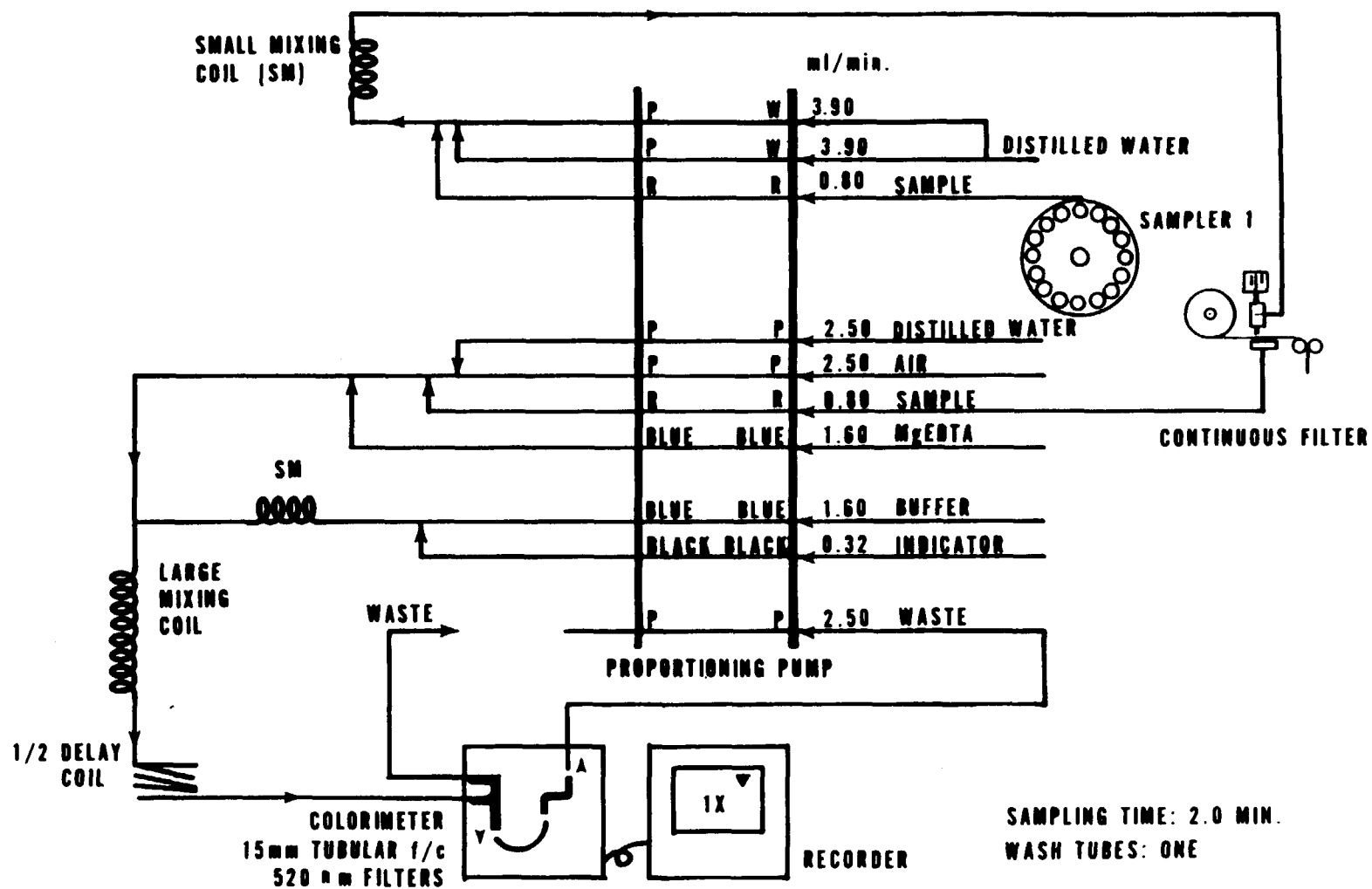


FIGURE 1. HARDNESS MANIFOLD AA-1

HARDNESS, Total (mg/1 as CaCO₃)
Method 130.2 (Titrimetric, EDTA)

STORET NO. 00900

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg CaCO₃.
 - 1.3 Automated titration may be used.
2. Summary of Method
 - 2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na₂EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.
3. Sample Handling and Preservation
 - 3.1 Cool to 4°C, HNO₃ to pH < 2.
4. Comments
 - 4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.
 - 4.1.1 Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.
5. Apparatus
 - 5.1 Standard laboratory titrimetric equipment.
6. Reagents
 - 6.1 Buffer solution
 - 6.1.1 If magnesium EDTA is available: Dissolve; 16.9 g NH₄Cl in 143 ml conc. NH₄OH in a 250 ml volumetric, add 1.25 g of magnesium salt of EDTA and dilute to the mark with distilled water. Then go to 6.1.3.
 - 6.1.2 If magnesium EDTA is unavailable: Dissolve 1.179 g disodium EDTA (analytical reagent grade) and 780 mg MgSO₄•7H₂O (or 644 mg MgCl₂•6H₂O) in 50 ml distilled water. Add this solution to a 250 ml volumetric flask containing 16.9 g NH₄Cl and 143 ml conc. NH₄OH with mixing and dilute to the mark with distilled water.
 - 6.1.3 Store in a tightly stoppered plastic bottle; stable for approximately one month. Dispense with bulb operated pipet. Discard when 1 or 2 ml added to sample fails to produce a pH of 10.0 ±0.1 at end point of titration.

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Editorial revision 1978 and 1982

- 6.1.4 Commercially available "odorless buffers" which are more stable, may be used.
- 6.2 Inhibitors: For most waters inhibitors are not necessary. If interfering ions are present use one of the following:
- 6.2.1 Inhibitor I: NaCN powder. (Caution: extremely poisonous). Flush solutions or sample containing this down drain using large quantities of water. Make sure no acids are present which might liberate HCN gas.
- 6.2.2 Inhibitor II: Dissolve 5.0 g $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ or 3.7 g $\text{Na}_2\text{S} \cdot 5 \text{H}_2\text{O}$ in 100 ml distilled water. Exclude air with tightly fitted rubber stopper. This gives sulfide precipitates which may obscure the end point if large quantities of heavy metals are present. Deteriorates rapidly through air oxidation.
- 6.2.3 Inhibitor III: Dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol or isopropanol.
- 6.3 Indicator: Use a commercially available indicator such as Calmagite indicator (Mallinckrodt) or one of the formulations described below (6.3.1–6.3.3)
- 6.3.1 Mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 ml of 95% ethanol or isopropanol.
- 6.3.2 Dissolve 0.5 to 1.0 g Eriochrome Black T in an appropriate solvent such as triethanolamine or 2-methoxyethanol. Stable approximately one week.
- 6.3.3 Mix together 0.5 g Eriochrome Black T and 100 g NaCl.
- 6.4 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $\text{Na}_2\text{H}_2\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 \cdot 2 \text{H}_2\text{O}$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (6.4.1) by titration (6.4.5). Store in polyethylene. Check periodically because of gradual deterioration.
- 6.4.1 Standard calcium solution 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in metals) in a 500 ml flask. Add, a little at a time, 1 + 1 HCL (6.4.2) until all of the CaCO_3 has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2 . Cool. Add a few drops of methyl red indicator (6.4.3) and adjust to intermediate orange color by adding 3N NH_4OH (6.4.4) or 1 + 1 HCl (6.4.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.
- 6.4.2 Hydrochloric acid solution, 1 + 1.
- 6.4.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml volumetric flask and dilute to the mark.
- 6.4.4 Ammonium hydroxide solution, 3 N: Dilute 210 ml of conc. NH_4OH to 1 liter with distilled water.
- 6.4.5 Standardization titration procedure: Place 10.0 ml standard calcium solution (6.4.1) in vessel containing about 50 ml distilled water. Add 1 ml buffer solution (6.1). Add 1–2 drops indicator (6.3) or small scoop of dry indicator (6.3.3). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last

few drops at 3–5 second intervals. At end point the color is blue. Total titration duration should be 5 minutes from the time of buffer addition.

$$N \text{ of EDTA} = \frac{0.2}{\text{ml of EDTA}}$$

6.5 Ammonium Hydroxide, 1N: Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water.

7. Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Titration of sample-normal to high hardness:

7.2.1 Sample should require < 15 ml EDTA titrant (6.4) and titration should be completed within 5 minutes of buffer addition.

7.2.2 Place 25.0 ml sample in titration vessels, neutralize with 1N ammonium hydroxide (6.5) and dilute to about 50 ml.

7.2.3 Add 1 to 2 ml buffer solution (6.1).

7.2.4 If end point is not sharp (as determined by practice run) add inhibitor at this point (see 7.4).

7.2.5 Add 1 to 2 drops indicator solution (6.3.1 or 6.3.2) or small scoop of dried powder indicator formulation (6.3.3).

7.2.6 Titrate slowly with continuous stirring with standard EDTA titrant (6.4) until last reddish tint disappears. Solution is normally blue at end point.

7.3 Titration of sample-low hardness (less than 5 mg/l)

7.3.1 Use a larger sample (100 ml)

7.3.2 Use proportionately larger amounts of buffer, inhibitor and indicator

7.3.3 Use a microburet and run a blank using redistilled, distilled or deionized water.

7.4 To correct for interferences:

7.4.1 Some metal ions interfere by causing fading or indistinct end points. Inhibitors reduce this in accord with the scheme below for 25.0 ml samples diluted to 50 ml.

**Maximum Concentrations of Interferences Permissible
with Various Inhibitors^a**

Interfering Substance	Maximum Interference Concentration mg/l		
	Inhibitor I	Inhibitor II	Inhibitor III
Aluminum	20	20	20
Barium	b	b	b
Cadmium	b	20	b
Cobalt	over 20	0.3	0 ^c
Copper	over 30	20	0.3
Iron	over 30	5	20
Lead	b	20	b
Manganese (Mn ²⁺)	b	1	1
Nickel	over 20	0.3	0 ^c
Strontium	b	b	b
Zinc	b	200	b
Polyphosphate		10	

a Based on 25-ml sample diluted to 50 ml.

b Titrates as hardness.

c Inhibitor fails if substance is present.

7.4.2 Inhibitor I: At step 7.2.4 add 250 mg NaCN. Add sufficient buffer to achieve pH 10.0 ± 0.1 to offset alkalinity resulting from hydrolysis of sodium cyanide.

7.4.3 Inhibitor II: At step 7.2.4 add 1 ml of inhibitor II (6.2.2)

7.4.4 Inhibitor III: At step 7.2.4 add 1 ml of inhibitor III (6.2.3).

8. Calculations:

$$\text{Hardness (EDTA)} \left[\frac{\text{mg CaCO}_3}{\text{l}} \right] = \frac{A \times N \times 50,000}{\text{ml sample}}$$

where:

A = ml EDTA titrant (6.4)

N = normality of EDTA titrant.

9. Precision and Accuracy

9.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

<u>Increment as Total Hardness mg/liter, CaCO₃</u>	<u>Precision as Standard Deviation mg/liter, CaCO₃</u>	<u>Bias, %</u>	<u>Accuracy as Bias, mg/liter, CaCO₃</u>
31	2.87	-0.87	-0.003
33	2.52	-0.73	-0.24
182	4.87	-0.19	-0.4
194	2.98	-1.04	-2.0
417	9.65	-3.35	-13.0
444	9.73	-3.23	-14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

- 9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 194 mg CaCO₃/l, the standard deviation was ± 3 .
- 9.3 A synthetic unknown sample containing 610 mg/l total hardness as CaCO₃ contributed by 108 mg/l Ca and 82 mg/l Mg, and the following supplementary substances: 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.25 mg/l nitrite N, 1.1 mg/l nitrate N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity (contributed by NaHCO₃) in distilled water was analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1126-67, p 161, Method B (1976).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology and Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis of Water samples for Nitrite - Nitrate Nitrogen and Nitrite-Nitrogen (as mg/l N).

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks, will be collected. One of the 3 samples will be a potentially high concentration leachate samples, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May of 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May of 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples must be analyzed within 28 days of sample collection and reported within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use one of the following methods:

- a) U.S. EPA Method 353.2, "Nitrogen, Nitrate - Nitrite (Colorimetric, Automated, Cadmium Reduction," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- b) U.S. EPA Method 353.3, "Nitrogen, Nitrate - Nitrite (Spectrometric, Manual, Cadmium Reduction," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) Store samples at 4°C until analysis and validation of results.
- b) The analytical working range of the shall not exceed 0.1 to 10.0 mg/l.
- c) Check the sample pH (with wide range pH paper). If the pH > 2, contact Region 5 CPMS/CRL for instructions.
- d) Use only the methods specified in Item 7. Obtain approval from Region 5 CPMS/CRL before using any other method.
- e) For Methods 353.2 and 353.3; after checking the pH, check for residual chlorine (or oxidizers) and sulfide using test strips (such as Starch/Iodide & Lead Acetate paper). Contact Region 5 CPMS/CRL if these interferences are present; however, the laboratory must remove these interferences before analysis.
- f) The lab must also minimize interferences due to metals, in order to prolong column life (see Section 7.1.2 of Method 353.3).
- g) The lab may dilute the samples up to 10:1 prior to analysis (Section 7.4 of Method 353.3), provided that the final results do not exceed the 0.1 - 10.0 mg/l calibration range.

- h) Neutralize all samples to pH 5 - 9 (or phenolphthalein color endpoint) prior to analysis.
- i) Dilute and re analyze the neutralized sample if the concentrations exceed that of the highest standard.
- j) Use at least 5 calibration standards (including a zero level standard).
- k) Prepare the lab blank using 1 ml/l of H₂SO₄. Neutralize and analyze like a sample.
- l) Store samples at 4°C until analysis and validation of results.

9 Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Report results as "mg/l Nitrate-Nitrite Nitrogen as N" and "mg/l Nitrite-Nitrogen as N".
- b) Clearly identify the test procedure used.
- c) All bench records, tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, duplicates, etc., with resulting absorbencies or concentration readouts, will be provided.
- d) Any sample treatment to remove interferences will be documented.
- e) The lab shall submit photocopies of the instrument readouts (strip charts, printer tapes, etc.)
- f) All records must be clear, legible, and complete enough to recalculate all concentrations.
- g) EPA QC Reference Samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values, along with 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Nitrite-Nitrate Nitrogen	0.10 mg/l as N	± 10% or ± 0.1 mg/l N
Nitrite Nitrogen	0.10 mg/l as N	± 10% or ± 0.1 mg/l N

NOTE: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audit</u>	<u>Limits</u>
Matix Spike ¹	1 in 10 samples, or at least 1	85-115% R
Lab Dulicate	1 in 10 samples, or at least 1	± 10% or ± 0.1 mg/l difference
Lab Blank (w/ 1 ml H ₂ SO ₄)	2 per sample set	<0.1 mg/l N
Calibration Verifi- cation Standard	1 in 10 samples, or at least 1	90-110% true
Calibration Blank	1 in 10 samples or at least 1	<0.1 mg/l N
Set of EPA Nutrient QC Reference Samples ²	1 in 10 samples or	85-115% true

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

¹ Matrix Spike Concentrations will be 30%, or larger, of sample concentration, but spiked samples must not exceed the working range of the standard curve.

² Concentration 1 & 2, or EPA F/NO₃ QC Sample, WS Series concentration 1 & 2.

NITROGEN, NITRATE-NITRITE

Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
 - 1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
 - 2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
 - 3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H₂SO₄ per liter) and refrigeration.
Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
 - 4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered.
 - 4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
 - 4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
5. Apparatus
 - 5.1 Technicon AutoAnalyzer (AAI or AAI) consisting of the following components:
 - 5.1.1 Sampler.
 - 5.1.2 Manifold (AAI) or analytical cartridge (AAII).
 - 5.1.3 Proportioning Pump
 - 5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
 - 5.1.5 Recorder.

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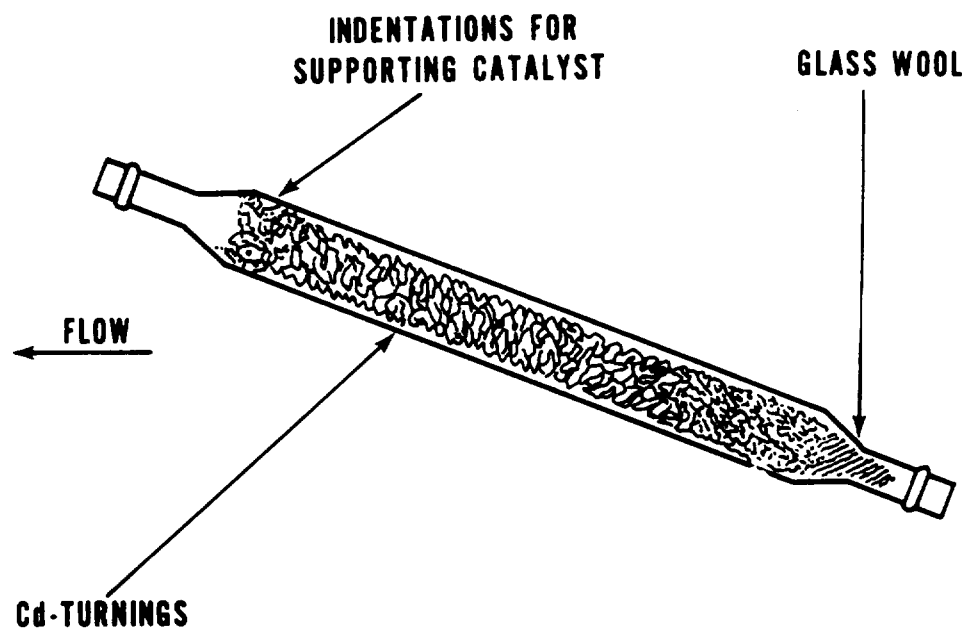
Editorial revision 1974 and 1978

5.1.6 Digital printer for AAI (Optional).

6. Reagents

- 6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).
- 6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:
 - 6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.
 - 6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.
 - 6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.
- 6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.
- 6.4 Preparation of reduction column AAI: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper-cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.

NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.
- 6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.
- 6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.
- 6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.
- 6.8 Copper sulfate solution, 2%: Dissolve 20 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 500 ml of distilled water and dilute to 1 liter.
- 6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with H_2SO_4 , use 2 ml H_2SO_4 per liter of wash water.
- 6.10 Ammonium chloride-EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 ml Brij-35 (available from Technicon Corporation).



TILT COLUMN TO 20° POSITION

**FIGURE 1. COPPER CADMIUM REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)**

- 6.11 Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg $\text{NO}_3\text{-N}$.
- 6.12 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg $\text{NO}_2\text{-N}$.
- 6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg $\text{NO}_3\text{-N}$. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.
- 6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg $\text{NO}_2\text{-N}$. Solution is unstable; prepare as required.
- 6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

<u>Conc., mg$\text{NO}_2\text{-N}$ or $\text{NO}_3\text{-N/l}$</u>	<u>ml Standard Solution/100 ml</u>
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl - 24.53 g/l	MgCl_2 - 5.20 g/l	Na_2SO_4 - 4.09 g/l
CaCl_2 - 1.16 g/l	KCl - 0.70 g/l	NaHCO_3 - 0.20 g/l
KBr - 0.10 g/l	H_3BO_3 - 0.03 g/l	SrCl_2 - 0.03 g/l
NaF - 0.003 g/l		

7. Procedure

- 7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH .
- 7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20° incline position (AAI). Care should be taken not to introduce air into reduction column on the AAI.
- 7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.
- NOTE 3:** Condition column by running 1 mg/l standard for 10 minutes if a new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

- 7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.
- 7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAI, use a 40/hr, 4:1 cam and a common wash.
- 7.6 Switch sample line to sampler and start analysis.
8. Calculations
 - 8.1 Prepare appropriate standard curve or curves derived from processing NO₂ and/or NO₃ standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.
9. Precision and Accuracy
 - 9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as	
		Bias, %	Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	- 2.69	-0.067

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3. Annual Book of ASTM Standards, Part 31, "Water", Standard D1254, p 366 (1976).
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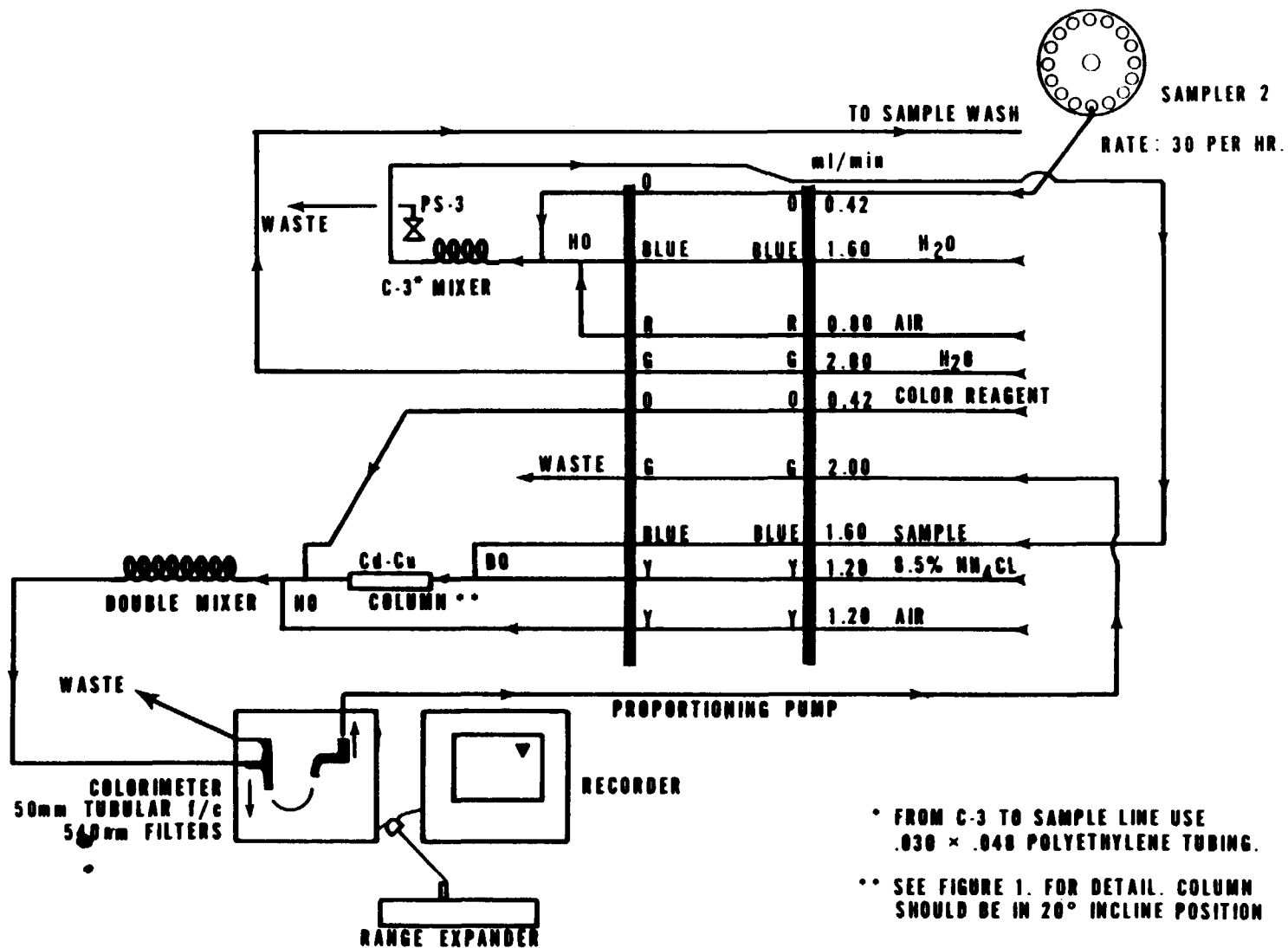


FIGURE 2. NITRATE - NITRITE MANIFOLD AA-1

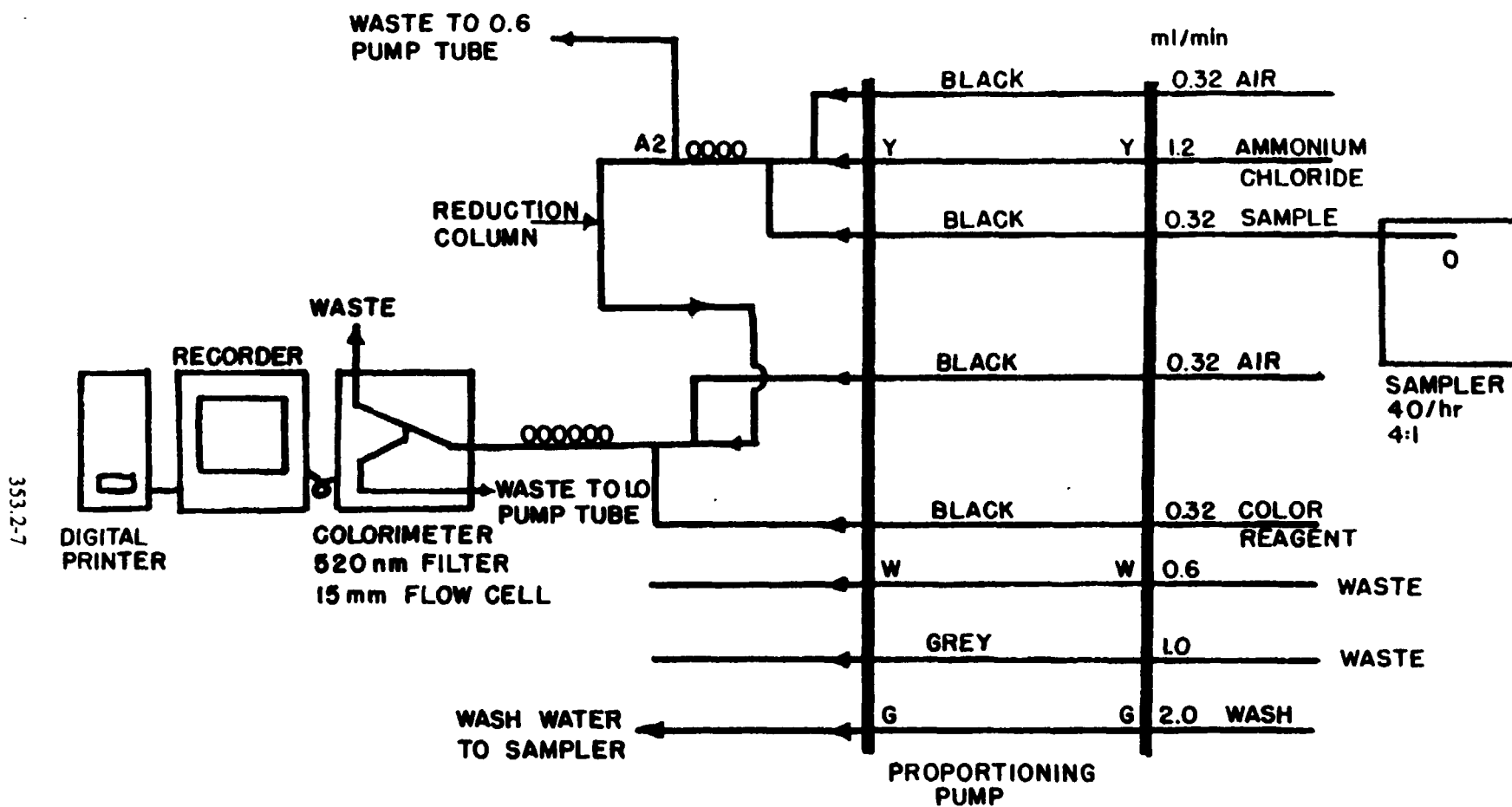


FIGURE 3 NITRATE-NITRITE MANIFOLD AA II

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
 - 1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
 - 2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
 - 3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H₂SO₄ per liter) and refrigeration.
Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
 - 4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45 μ membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.
 - 4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
 - 4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
 - 4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

Approved for NPDES and SDWA
Issued 1974

5. Apparatus
 - 5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.
 - 5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.
6. Reagents
 - 6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).
 - 6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:
 - 6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.
 - 6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.
 - 6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.
 - 6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/1 $\text{NO}_3\text{-N}$ standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.
 - 6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.
 - 6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.
 - 6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)-ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.
 - 6.7 Zinc sulfate solution: Dissolve 100 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and dilute to 1 liter.
 - 6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.
 - 6.9 Ammonium hydroxide, conc.
 - 6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.
 - 6.11 Copper sulfate solution, 2%: Dissolve 20 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 500 ml of distilled water and dilute to 1 liter.
 - 6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg $\text{NO}_3\text{-N}$.

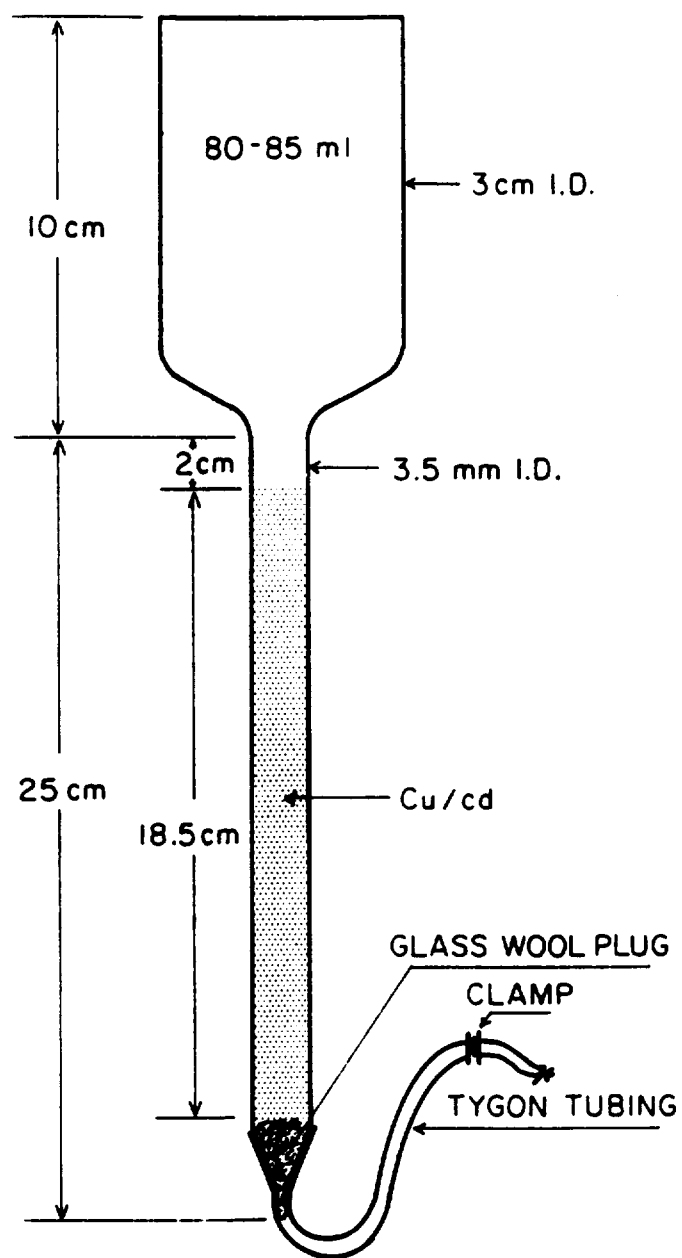


FIGURE 1. REDUCTION COLUMN

- 6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO₃-N.
- 6.14 Stock nitrite solution: Dissolve 6.072 g KNO₂ in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO₂-N.
- 6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO₂-N.
- 6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

<u>Conc., mg-NO₃-N/l</u>	<u>ml of Standard Solution/100.0 ml</u>
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

- 7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.
 - 7.1.1 Filter sample through a glass fiber filter or a 0.45 μ membrane filter.
 - 7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4–0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45 μ membrane filter.
- 7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).
- 7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH₄OH. This is done to insure a sample pH of 8.5 after step 7.4.
- 7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.
- 7.5 Pour sample into column and collect sample at a rate of 7–10 ml per minute.
- 7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.
- 7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg NO₃-N/l, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

- 7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.
8. Calculation
 - 8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against $\text{NO}_3\text{-N}$ mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.
 - 8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mgNO}_2 + \text{NO}_3 - \text{N/l} = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy
 - 9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $\text{NO}_3 + \text{NO}_2\text{-N/l}$, the standard deviations were ± 0.005 , ± 0.004 , ± 0.005 and ± 0.01 , respectively.
 - 9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $\text{NO}_3 + \text{NO}_2\text{-N/l}$, the recoveries were 100%, 102% and 100%, respectively.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 423, Method 419C (1975).
2. Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts". Analyst, May 1970, Vol. 95, p 514-518.
3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p 133-145.
4. Brewer, P. G., Riley, J. P., "The Automatic Determination of Nitrate in Sea Water", Deep Sea Research, 1965, Vol. 12, p 765-772.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

A. EPA Region/Client: Region V / Ecology and Environment, Inc.

B. RSCC Representative: Jan Pels

C. Telephone Number: 312-353-2720

D. Date of Request: November 18, 1992

E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis for Sulfate as mg/l SO₄ in water.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks, will be collected. One of three 3 samples will be a potentially high level leachate sample, the other 2 will be groundwater monitoring well samples.

3. Purpose of analysis (specify whether Superfund [enforcement or remedial action], RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May of 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May of 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples must be analyzed within 28 days of sample collection, and results reported within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Use one of the following attached methods:

- a) U.S. EPA Method 375.1 "Sulfate, (Colorimetric, Automated, Chloranilate)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- b) U.S. EPA Method 375.2 "Sulfate, (Colorimetric, Automated, Methylthymol Blue, AA II)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- c) U.S. EPA Method 375.3 "Sulfate (Gravimetric)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.
- d) U.S. EPA Method 375.4 "Sulfate (Turbidimeter)," from *Methods for Chemical Analysis of Water and Wastes*, 1983 edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) Store samples at 4°C until analysis and validation of results.
- b) For samples with >10 mg/l, method 375.3 is the method of choice.
- c) Use only the methods specified in Item 7. Obtain approval from CPMS, CRL before using any other method.
- d) The lab must also minimize interferences due to metals, organics, in order to achieve best results.
- e) Use at least 5 calibration standards (including a zero level standard).
- f) Store samples at 4°C until analysis and validation of results.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Report results as "mg/l Sulfate".
- b) Clearly identify the test procedure used.
- c) All bench records, tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, duplicates, etc., with resulting absorbances or concentration readouts, will be provided.
- d) Any sample treatment to remove interferences will be documented.
- e) The lab shall submit photocopies of the instrument readouts (strip charts, printer tapes, etc.)
- f) All records must be clear, legible, and complete enough to recalculate all concentrations.
- g) EPA QC Reference Samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values, along with 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Sulfate	1.0 mg/l	± 10% or ± 1.0 mg/l

NOTE: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
Lab Duplicate	1 per 10 samples, or at least 1	$\pm 10\%$ or ± 1.0 mg/l Difference
Lab Blank	1 per 10 samples, or at least 1	< 1.0 mg/l
Calibration Verification Std.	1 per sample set.	90 - 110% True

14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

SULFATE

Method 375.1 (Colorimetric, Automated, Chloranilate)

STORET NO. Total 00945

1. Scope and Application
 - 1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes, in the range of 10 to 400 mg SO₄/l. Approximately 15 samples per hour can be analyzed.
2. Summary of Method
 - 2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid is proportional to the amount of sulfate present.
3. Sample Handling and Preservation
 - 3.1 Refrigeration at 4°C.
4. Interferences
 - 4.1 Cations, such as calcium, aluminum, and iron, interfere by precipitating the chloranilate. These ions are removed automatically by passage through an ion exchange column.
5. Apparatus
 - 5.1 Technicon AutoAnalyzer consisting of:
 - 5.1.1 Sampler I.
 - 5.1.2 Continuous filter.
 - 5.1.3 Manifold.
 - 5.1.4 Proportioning pump.
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
 - 5.1.6 Recorder.
 - 5.1.7 Heating bath, 45°C.
 - 5.2 Magnetic stirrer.
6. Reagents
 - 6.1 Barium chloranilate: Add 9 g of barium chloranilate (BaC₆Cl₂O₄) to 333 ml of ethyl alcohol and dilute to 1 liter with distilled water.
 - 6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 ml of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.
 - 6.3 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.

NOTE 1: This solution is also used to clean out manifold system at end of sampling run.
 - 6.4 Ion exchange resin: Dowex-50 W-X8, ionic form-H⁺.

NOTE 2: Column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.

Issued 1971

375.1-1

6.5 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na_2SO_4 in distilled water and dilute to 1 liter in a volumetric flask. 1.0 ml = 1.0 mg.

6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

<u>ml of Stock Solution</u>	<u>Conc., mg/l</u>
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

7. Procedure

- 7.1 Set up manifold as shown in Figure 1. (Note that any precipitated BaSO_4 and the unused barium chloranilate are removed by filtration. If any BaSO_4 should come through the filter, it is complexed by the NaOH-EDTA reagent).
- 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.
- 7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.
- 7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.
- 7.5 Switch sample line from distilled water to sampler and begin analysis.

8. Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 39, 111, 188 and 294 mg SO_4/l , the standard deviations were ± 0.6 , ± 1.0 , ± 2.2 and ± 0.8 , respectively.
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 82 and 295 mg SO_4/l , recoveries were 99% and 102%, respectively.

Bibliography

1. Barney, J. E., and Bertolocini, R. J., Anal. Chem., 29, 283 (1957).
2. Gales, M. E., Jr., Kaylor, W. H. and Longbottom, J. E., "Determination of Sulphate by Automatic Colorimetric Analysis", Analyst, 93, 97 (1968).

375.1-3

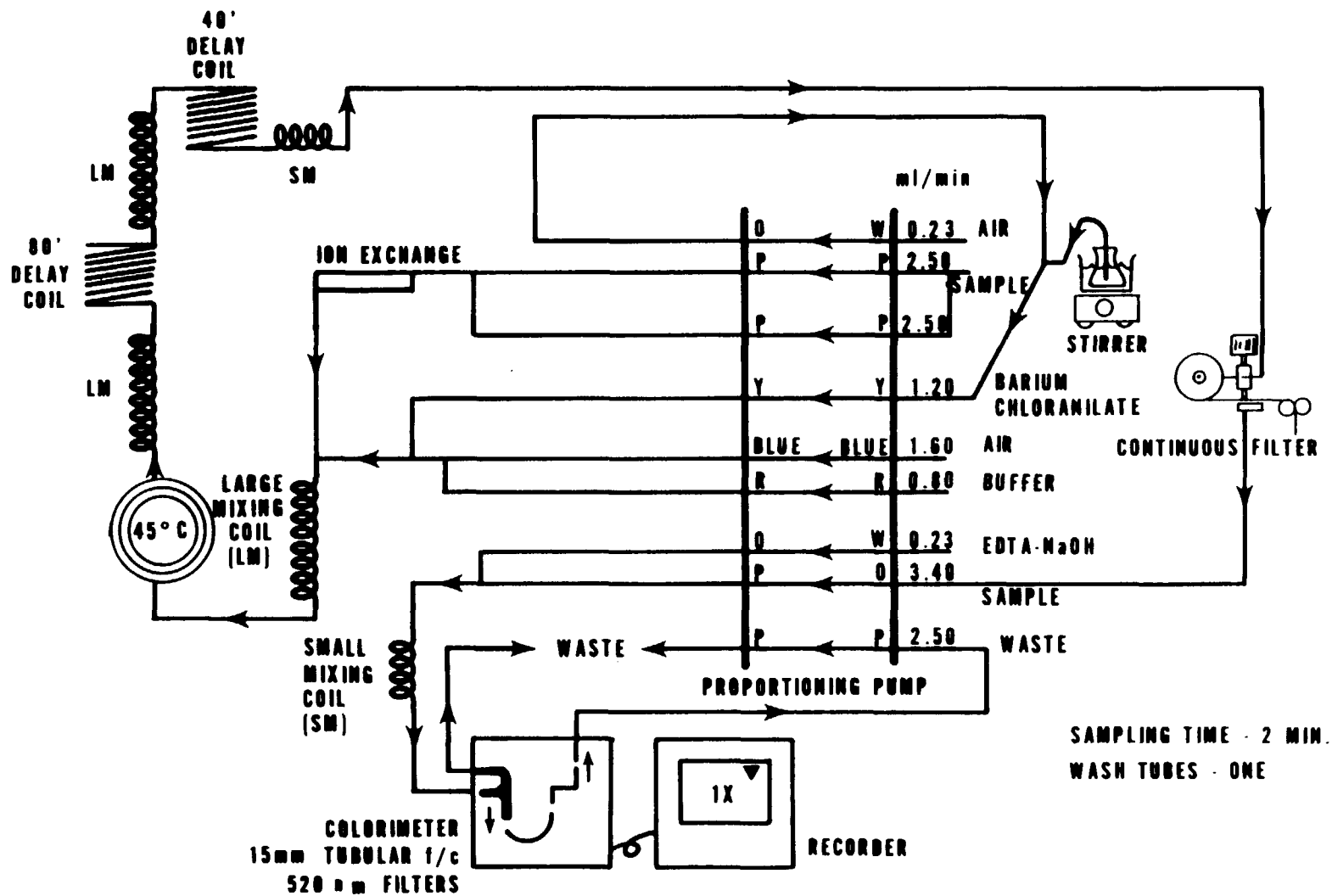


FIGURE 1 - SULFATE MANIFOLD AA-I

SULFATE

Method 375.2 (Colorimetric, Automated, Methylthymol Blue, AA II)

STORET NO. 00945

1. Scope and Application
 - 1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes.
 - 1.2 Samples in the range of 3 to 300 mg SO_4/l can be analyzed. The sensitivity of the method can be increased by a minor modification to analyze samples in the range of 0.5 to 30 mg SO_4/l . Approximately 30 samples per hour can be analyzed.
2. Summary of Method
 - 2.1 The sample is first passed through a sodium form cation-exchange column to remove multivalent metal ions. The sample containing sulfate is then reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at a pH of 2.5–3.0 to form barium sulfate. The combined solution is raised to a pH of 12.5–13.0 so that excess barium reacts with MTB. The uncomplexed MTB color is gray; if it is all chelated with barium, the color is blue. Initially, the barium and MTB are equimolar and equivalent to 300 mg SO_4/l ; thus the amount of uncomplexed MTB is equal to the sulfate present.
3. Sample Handling and Preservation
 - 3.1 Refrigeration at 4°C.
4. Interferences
 - 4.1 The ion exchange column eliminates interferences from multivalent cations. A mid-scale sulfate standard containing Ca^{++} should be analyzed periodically to insure that the column is functioning properly.
 - 4.2 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion exchange resin.
 - 4.3 Turbid samples should be filtered or centrifuged.
5. Apparatus
 - 5.1 Technicon Auto Analyzer consisting of:
 - 5.1.1 Sampler
 - 5.1.2 Manifold—high or low level (Figure I)
 - 5.1.3 Proportioning pump
 - 5.1.4 Colorimeter equipped with 15 mm flow cell and 460 nm interference filters.
 - 5.1.5 Recorder
 - 5.1.6 Digital Printer for AAII (optional)
6. Reagents
 - 6.1 Barium chloride: Dissolve 1.526 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 500 ml of distilled water and dilute to 1 liter.

Pending approval for NPDES
Issued 1978

- 6.2 Methylthymol blue: Dissolve 0.1182 g of methylthymol blue (3'3''-bis-N,N-bis carboxymethyl)-amino methylthymolsulfone-phthalein pentasodium salt) in 25 ml of barium chloride solution (6.1). Add 4 ml of 1.0 N hydrochloric acid which changes the color to bright orange. Add 71 ml of water and dilute to 500 ml with ethanol. The pH of this solution is 2.6. This reagent should be prepared the day before and stored in a brown plastic bottle in the refrigerator.
- 6.3 Buffer, pH 10.5 \pm 0.5: Dissolve 6.75 g of ammonium chloride in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide and dilute to one liter with distilled water.
- 6.4 Buffered EDTA: Dissolve 40 g of tetrasodium EDTA in pH 10.5 buffer (6.3), and dilute to one liter with buffer.
- 6.5 Sodium hydroxide solution, (50%): Dissolve 500 g NaOH in 600 ml of distilled water, cool, and dilute to 1 liter.
- 6.6 Sodium hydroxide, 0.18N: Dilute 14.4 ml of sodium hydroxide solution (6.5) to 1 liter.
- 6.7 Ion exchange resin: Bio-Rex 70, 20–50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of deionized water and decant the supernate before settling is complete.
- 6.8 Dilution Water: Add 0.75 ml of sulfate stock solution (6.9) and 3 drops of Brij-35 to 2 liters of distilled water.
- 6.9 Sulfate stock solution, 1 ml = 1 mg SO₄: Dissolve 1.479 g of dried (105°C) Na₂SO₄ in distilled water and dilute to 1 liter.
- 6.10 Dilute sulfate solution, 1 ml = 0.1 mg SO₄: Dilute 100 ml of sulfate stock solution (6.9) to 1 liter.
- 6.11 High level working standards, 10–300 mg/l: Prepare high level working standards by diluting the following volumes of stock standard (6.9) to 100 ml.

<u>ml stock</u>	<u>mg/l SO₄</u>
1	10
5	50
10	100
15	150
25	250
30	300

- 6.12 Low level working standards, 1–30 mg/l: Prepare low level working standards by diluting the following volumes of dilute sulfate solution (6.10) to 100 ml.

<u>ml stock</u>	<u>mg/l SO₄</u>
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

7. Procedure

- 7.1 Set up the manifold for high (0–300 mg SO₄/l) or low (0–30 mg SO₄/l) level samples as described in Figure I.
- 7.2 The ion exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5 inches long, 2.0 mm ID and 3.6 mm OD. This is conveniently done by using a pipet and a loose fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles to enter the column. If air bubbles become trapped, the column should be prepared over again. The column can exchange the equivalent of 35 mg of calcium. For the high level manifold this corresponds to about 900 samples with 200 mg/l Ca . The column should be prepared as often as necessary to assure that no more than 50% of its capacity is used up.
- 7.3 Allow the colorimeter, recorder and printer to warm up for 30 minutes. Pump all reagents until a stable baseline is achieved.
- 7.4 Analyze all working standards in duplicate at the beginning of a run to develop a standard curve. The A and B control standards are analyzed every hour to assure that the system remains properly calibrated. Since the chemistry is non-linear the 180 mg/l standard is set at 50% on the recorder using the standard calibration control on the colorimeter.
- 7.5 At the end of each day, the system should be washed with the buffered EDTA solution (6.4). This is done by placing the methylthymol blue line and the sodium hydroxide line in water for a few minutes and then in the buffered EDTA solution for 10 minutes. Wash the system with water for 15 minutes before shutting down.

8. Calculation

- 8.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with the standard curve.

9. Precision and Accuracy

- 9.1 In a single laboratory the estimated standard deviation, calculated from duplicate analyses of 26 surface and wastewaters at a mean concentration of 110 mg/l was ± 1.6 mg/l.
- 9.2 The mean recovery from 24 surface and wastewaters was 102%.

Bibliography

1. Lazrus, A.L., Hill, K.C. and Lodge, J.P., "Automation in Analytical Chemistry", Technicon Symposia, 1965.
2. Coloros, E., Panesar, M.R. and Parry, F.P., "Linearizing the Calibration Curve in Determination of Sulfate by the Methylthymol Blue Method", Anal. Chem. 48, 1693 (1976).

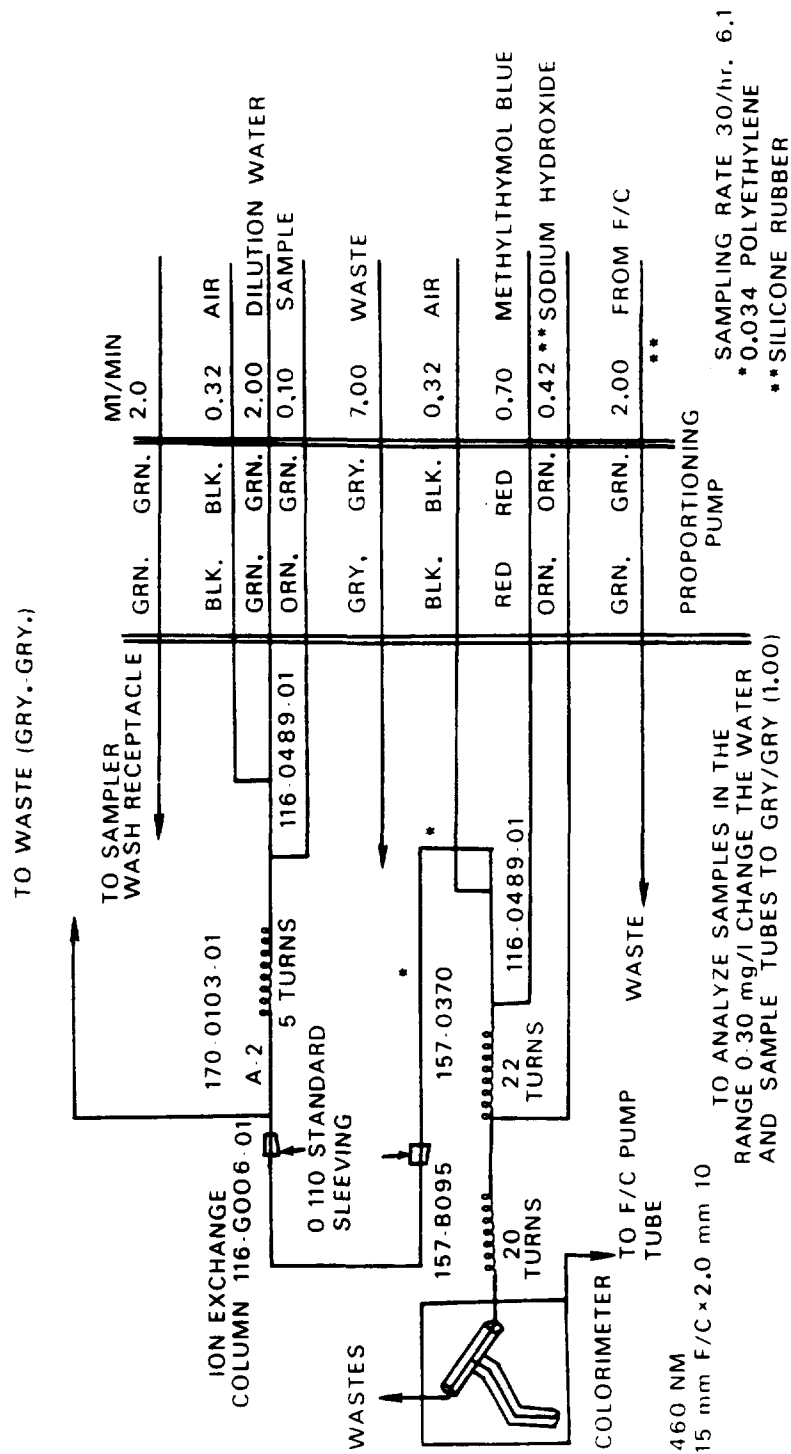


FIGURE 1 SULFATE MANIFOLD AA11

SULFATE

Method 375.3 (Gravimetric)

STORET NO. Total 00945

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface and saline water, domestic and industrial wastes.
 - 1.2 This method is the most accurate method for sulfate concentrations above 10 mg/l. Therefore, it should be used whenever results of the greatest accuracy are required.
2. Summary of Method
 - 2.1 Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as BaSO_4 .
 - 2.2 Preserve by refrigeration at 4°C.
3. Interferences
 - 3.1 High results may be obtained for samples that contain suspended matter, nitrate, sulfite and silica.
 - 3.2 Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Occlusion of alkali sulfate with barium sulfate causes the substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfate of alkali metal acts similarly and decomposes when heated. Heavy metals such as chromium and iron, cause low results by interfering with complete precipitation and by formation of heavy metal sulfates.
4. Apparatus
 - 4.1 Steam bath
 - 4.2 Drying oven, equipped with thermostatic control.
 - 4.3 Muffle furnace with heat indicator.
 - 4.4 Desiccator
 - 4.5 Analytical balance, capable of weighing to 0.1 mg.
 - 4.6 Filter paper, acid-washed, ashless hard-finish filter paper sufficiently retentive for fine precipitates.
5. Reagents
 - 5.1 Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water in a 100 ml volumetric flask and dilute to the mark with distilled water.
 - 5.2 Hydrochloric acid, HCl , 1 + 1
 - 5.3 Barium chloride solution: Dissolve 100 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 liter of distilled water. Filter through a membrane filter or hard-finish filter paper. One ml of this reagent is capable of precipitating approximately 40 mg SO_4 .

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- 5.4 Silver nitrate-nitric acid reagent: Dissolve 8.5 g AgNO_3 and 0.5 ml conc. HNO_3 in 500 ml distilled water.
6. Procedure
- 6.1 Removal of silica: If silica concentration is greater than 25 mg/l
- 6.1.1 Evaporate sample nearly to dryness in a platinum dish on a steam bath.
 - 6.1.2 Add 1 ml HCl solution (5.2), tilt dish and rotate until acid contacts all of the residue.
 - 6.1.3 Continue evaporation to dryness.
 - 6.1.4 Complete drying in an oven at 180°C.
 - 6.1.5 If organic matter present, char over a flame.
 - 6.1.6 Moisten with 2 ml distilled water and 1 ml HCl solution (5.2).
 - 6.1.7 Evaporate to dryness on a steam bath.
 - 6.1.8 Add 2 ml HCl solution (5.2).
 - 6.1.9 Take up soluble residue in hot distilled water and filter.
 - 6.1.10 Wash the insoluble silica with several small portions of hot distilled water.
 - 6.1.11 Combine filtrate and washings.
- 6.2 Precipitation of barium sulfate
- 6.2.1 If necessary, treat clarified sample to remove interfering agents.
 - 6.2.2 Adjust to contain approximately 50 mg SO_4 ion in a 250 ml volume.
 - 6.2.3 Adjust acidity with HCl solution (5.2) to pH 4.5 to 5.0, using pH meter or orange color of methyl red indicator (5.1).
 - 6.2.4 Add an additional 1 to 2 ml HCl solution (5.2).
 - 6.2.5 For lower concentrations of sulfate ion fix the total volume at 150 ml.
 - 6.2.6 Heat to boiling and, while stirring gently, add warm BaCl_2 solution (5.3) slowly, until precipitation appears to be complete; then add approximately 2 ml in excess.
 - 6.2.7 If amount of precipitate is small, add a total of 5 ml BaCl_2 solution (5.3).
 - 6.2.8 Digest the precipitate at 80 to 90°C preferably overnight but for not less than 2 hours.
- 6.3 Filtration and Weighing
- 6.3.1 Mix a little ashless filter paper pulp with the BaSO_4 and filter at room temperature.
 - 6.3.2 Wash the precipitate with small portions of warm distilled water until the washings are free of chloride as indicated by testing with silver nitrate-nitric acid reagent (5.4).
 - 6.3.3 Dry the filter and precipitate.
 - 6.3.4 Ignite at 800°C for 1 hour. DO NOT LET THE FILTER PAPER FLAME.
 - 6.3.5 Cool in a desiccator and weigh.
7. Calculation

$$\text{mg/l SO}_4 = \frac{\text{mg BaSO}_4 \times 411.5}{\text{ml sample}}$$

8. **Precision and Accuracy**

- 8.1 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 250 ug/l nitrite N, 1.1 mg/l nitrate N and 42.5 mg/l alkalinity (contributed by NaHCO_3), was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516-68, Method A, p 429 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 493, Method 427A, (1975).

SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

1. Scope and Application
 - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4 /l.
 - 1.3 The minimum detectable limit is approximately 1 mg/l sulfate.
2. Summary of Method
 - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
 - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
 - 2.3 Silica in concentrations over 500 mg/l will interfere.
3. Comments
 - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
 - 3.2 Preserve by refrigeration at 4°C.
4. Apparatus
 - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
 - 4.2 Photometer: one of the following which are given in order of preference.
 - 4.2.1 Nephelometer
 - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
 - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
 - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
 - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. Reagents
 - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
 - 5.2 Barium chloride, BaCl_2 , crystals, 20 to 30 mesh.
 - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

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5.4 Standard sulfate solution (1.00 ml = 100 μ g SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter

B = ml Na_2CO_3 solution

C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4 : Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of BaCl_2 crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minutes at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.

6.3.1 Prepare calibration curve using standard sulfate solution (5.4).

6.3.2 Space standards at 5 mg/l increments in the 0–40 mg/l sulfate range.

- 6.3.3 Above 50 mg/l the accuracy decreases and the suspensions lose stability.
- 6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.
- 6.4 Correction for sample color and turbidity.
- 6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).
7. Calculations
- 7.1 Read mg SO₄ from calibration curve

$$\text{mg SO}_4/\text{l} = \frac{\text{mg SO}_4 \times 1,000}{\text{ml sample}}$$

8. Precision and Accuracy
- 8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as	
		Bias, %	Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

- 8.2 A synthetic unknown sample containing 259 mg/l sulfate, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/l Na, 241 mg/l chloride, 0.250 mg/l nitrite N, 1.1 mg/l nitrate N, and 42.5 mg/l total alkalinity (contributed by NaHCO₃) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516-68, Method B, p 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 496, Method 427C, (1975).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology and Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis of Total Dissolved Solids (180°C) in Water. Results are to be reported as mg/l dissolved solids.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 samples, plus 3 field duplicates and 3 field blanks, will be collected. One of the 3 samples will be potentially high concentration leachate samples, the remaining 2 will be groundwater samples.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial Activity

4. Estimated date(s) of collection:

Samples will be collected during the months of March - May of 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March - May of 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples must be analyzed within 7 days of sample collection. All results must be submitted within 30 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

One of the following methods must be used in the analysis:

- a) U.S. EPA method 160.1 from *Methods for Chemical Analysis of Water and Wastes*, 1983.
- b) Method 209B from *Standard Methods for the Examination of Water and Wastewater*, 16th edition.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) Use standard aliquots of 100 ml; however, do not use sample aliquots yielding more than 200 mg residue. If residue is greater than 200 mg, repeat the analysis using a smaller aliquot.
- b) If the pH value is less than 4.0, raise the pH of the aliquot (using NaOH titrant) to between pH 4 and 8, and subtract the weight of sodium added from the weight of the residue.
- c) Residue will be weighed either to a constant weight pursuant to section 7.6 of Method 160.1, the final weight is used for the calculations. Constant weight is defined as:
 - 1) Less than 0.5 mg or less than 4% weight loss from the previous weight, whichever is smaller, or;
 - 2) Dried overnight (12 hour drying time) with a single weight used for calculations.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):

- a) Identify the QC reference sample lot numbers used and their

- "true" or target values, with 95% confidence intervals.
- b) Bench Records of tare weights, final weights, additional weights to determine constant weights, volumes filtered, blanks, duplicates samples, and reference samples will be provided with copies of all worksheets used to calculate results.
 - c) Dates and times of (1) determinations of tare weights, (2) sample filtration, and (3) determination of residue weights and constant residue weights will be part of the bench records.
 - d) All records of analyses must be legible and sufficient to recalculate all sample concentration and QA results.

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and originals of data to the Region in the time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter</u>	<u>Detection Limits</u>	<u>Precision Desired</u>
Total Dissolved Solids (TDS)	20 mg/l	< 2 mg difference in duplicate sample aliquots for values < 200 mg/l, or <10% for values > 200 mg/l

NOTE: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits</u>
1 set of U.S. EPA QC Mineral Reference Samples - 2 concentration levels.	1 per sample set.	85 - 115% Recovery

Laboratory Duplicate	At least 1 per group of 10 or fewer samples.	$\pm 10\%$ or ± 2 mg of residue (whichever is greater).
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Laboratory Blank (100 ml of filtered reagent water)	At least 1 per group of 10 or fewer samples.	- 20 mg/l to + 20 mg/l
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14. Action required if limits are exceeded:

Contact SMO for corrective action and re analysis.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

RESIDUE, FILTERABLE

Method 160.1 (Gravimetric, Dried at 180°C)

STORET NO. 70300

1. Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The practical range of the determination is 10 mg/l to 20,000 mg/l.
2. Summary of Method
 - 2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
 - 2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.
3. Definitions
 - 3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
 - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
 - 5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
 - 5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
 - 5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
 - 6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
 - 6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
 - 6.3 Suction flask, 500 ml.
 - 6.4 Gooch crucibles, 25 ml (if 2.1 cm filter is used).
 - 6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).
 - 6.6 Steam bath.
 - 6.7 Drying oven, 180°C \pm 2°C.
 - 6.8 Desiccator.

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Issued 1971

- 6.9 Analytical balance, capable of weighing to 0.1 mg.
7. Procedure
- 7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.
 - 7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to $550 \pm 50^{\circ}\text{C}$ for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to $180 \pm 2^{\circ}\text{C}$ for one hour. Cool in desiccator and store until needed. Weigh immediately before use.
 - 7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.
 - 7.4 Filter the sample through the glass fiber filter, rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.
 - 7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.
 - 7.6 Dry the evaporated sample for at least one hour at $180 \pm 2^{\circ}\text{C}$. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.
8. Calculation
- 8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/l} = \frac{(A - B) \times 1,000}{C}$$

where:

A = weight of dried residue + dish in mg

B = weight of dish in mg

C = volume of sample used in ml

9. Precision and Accuracy
- 9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology & Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis for Total Organic Carbon in Water. Most samples will be unfiltered, although certain aliquots can be filtered and preserved at the time of collection. Results are reported as mg/l C.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 3 water samples, plus 3 field duplicates and 3 field blanks, will be collected. One of the 3 samples will be potentially high concentration leachate samples, the remainder will be groundwater samples from monitoring wells.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial action

4. Estimated date(s) of collection:

Samples will be collected during the months of March 1993 - May 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March 1993 - May 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples should be analyzed as soon as possible, but not to exceed 28 days from sample collection. Laboratory must report results within 30 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Samples will be analyzed by U.S. EPA method 415.1 "Organic Carbon, Total (Combustion or Oxidation)", from *Methods for Chemical Analysis of Water and Wastes*. Samples will be preserved with HCl or H₂SO₄ to pH <2. Samples will be stored at 4°C until analysis and validation of results.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

- a) Check sample pH (w/ wide range pH paper). If pH >2, contact CPMS, CRL for instructions.
- b) The holding time is not to exceed 28 days from sample collection.
- c) Homogenize samples if necessary.
- d) Qualify results where suspended solids content may affect accuracy.
- e) Instruments with syringe injection will utilize 2 injections per measurement. If the 2 injections differ by more than 10% or 2 mg/l (which ever is greater), repeat and report the average of 4 injections.
- f) Inorganic carbon will be purged from solution or, if determined separately, subtracted from the Total Carbon values.
- g) The calibration curve must include at least 5 standards, and one of the standards must be zero concentration.
- h) Obtain approval of Region 5 CPMS/CRL prior to use of any other method.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):
- a) Test procedures and specific instrument used will be clearly identified.
 - b) Bench records tabulating the order of calibration standards, lab blanks, lab duplicates, samples, lab control standards, spikes, etc., with resulting output on concentration readout will be provided, along with worksheets used to calculate results.
 - c) Specify the organic compound used to prepare standards and spikes.
 - d) A photocopy of the instrument readout, (i.e. strip charts, printer, tapes, etc.) must be included.
 - e) Results are to be reported in mg/l C.
 - f) Records of analysis and calculations must be legible and sufficient to recalculate all concentrations.
 - g) U.S. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values with 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and original data to Region time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter:</u>	<u>Detection Limit(s)</u>	<u>Precision Desired</u>
Total Organic Carbon (TOC)	2 mg/l	Difference in duplicate results should not exceed $\pm 10\%$ for concentrations >20 mg/l or ± 2 mg/l for concentrations <20 mg/l.

NOTE: These are minimum requirements. Report the actual detection limits used, based on the specified methodologies.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits*</u>
Matrix Spike*	at least 1 per group of 10 or fewer samples.	85 - 115%
Lab Duplicate	at least 1 per group of 10 or fewer samples.	$\pm 10\%$ or ± 2.0 mg/l
Lab Blank	at least 1 per group of 10 or fewer samples.	≤ 2.0 mg/l
Calibration Verification Standard	1 per group of 10 or fewer samples, and at end of set.	90 - 110%
1 set of U.S. EPA demand QC reference samples (conc. 1 and 2)	1 per sample set.	85 - 115%

*The Matrix Spike concentrations will be approximately 30% of sample concentrations, but spikes samples shall not exceed the working range of the standard curve.

NOTE: Do not use designated field blanks for QA audits.

14. Action required if limits are exceeded:

Take Corrective action and re analyze samples - Contact SMO immediately.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office (SMO).

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680

Dissolved 00681

1. Scope and Application
 - 1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
 - 1.2 The method is most applicable to measurement of organic carbon above 1 mg/l.
2. Summary of Method
 - 2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
 - 3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
 - A) soluble, nonvolatile organic carbon; for instance, natural sugars.
 - B) soluble, volatile organic carbon; for instance, mercaptans.
 - C) insoluble, partially volatile carbon; for instance, oils.
 - D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
 - E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
 - 3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

Approved for NPDES

Issued 1971

Editorial revision 1974

4. Sample Handling and Preservation
 - 4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.
 - 4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.
 - 4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($\text{pH} \leq 2$) with HCl or H_2SO_4 .
5. Interferences
 - 5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.
 - 5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.
6. Apparatus
 - 6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.
 - 6.2 Apparatus for total and dissolved organic carbon:
 - 6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.
 - 6.2.2 No specific analyzer is recommended as superior.
7. Reagents
 - 7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.
 - 7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.
 - 7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.
 - 7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

- 7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.
- NOTE 3:** This standard is not required by some instruments.
- 7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.
8. Procedure
- 8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.
- 8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.
9. Precision and Accuracy
- 9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+ 15.27	+ 0.75
107	8.32	+ 1.01	+ 1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574-79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS NUMBER

Approved By: SPECIAL ANALYTICAL SERVICE
Client Request

☐ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V / Ecology & Environment, Inc.
B. RSCC Representative: Jan Pels
C. Telephone Number: 312-353-2720
D. Date of Request: November 18, 1992
E. Site Name: H.O.D. Landfill

Please provide below description for your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheet(s) or attach supplementary information as needed.

1. General description of analytical service request:

Analysis for Total Organic Carbon in Soil/Sediment (air dried, all soil screened through 100 or 140 mesh). Results are reported as %C.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediment; and whether low, medium, or high concentrations):

A total of 1 soil/sediment sample, plus 1 field duplicate, will be collected. Concentrations may range from 0.1% C to 10.0% C, or more.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

SUPERFUND - Remedial action

4. Estimated date(s) of collection:

Samples will be collected during the months of March 1993 - May 1993.

5. Estimated date(s) and methods of shipment:

Samples will be shipped during the months of March 1993 - May 1993, by Federal Express overnight delivery.

6. Number of days analysis and data required after laboratory receipt of sample(s):

Samples should be analyzed within 28 days of receipt. Laboratory must report results within 30 days of receipt of final sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Determination of Organic Carbon (%) in Soil. Use only the methods listed below, from *Methods of Soil Analyses, Part II - Chemical and Microbiological Properties*, 2nd edition, 1982, American Society of Agronomy and Soil Society of America, Madison, Wisconsin. Copies of this copyrighted material are not provided, because no laboratory doing organic carbon analysis of soils should be without it.

- a) Sample Preparation: Representative sub-aliquot of air dried soil screened through 100 or 140 mesh, as appropriate. All of the sub-aliquot must pass this screen.
- b) Test for Presence of Inorganic Carbon, MSA, Part II, Section 29-3.3.1. Place finely ground soil on a spot plate, and moisten with a few drops of water. Add 4 N HCl dropwise to the wetted sample and observe any effervescence. Allow sufficient time for dolomite to react (-5 min.). If inorganic carbon is absent, proceed with Total Carbon in Items 7c or 7d below. If inorganic carbon is present, or if the test is not definitive, proceed with Items 7e or 7f prior to Total Carbon measurements of Item 7c or 7d.
- c) Total Carbon (Dry Combustion), MSA, Part II, Section 29-2.2.2. Use this as a guide for instrument specifications. Instrument must test solid samples directly. Illustrative examples of this methodology are:
 - 1) Total Carbon (Dry Combustion - Medium Temperature Resistance Furnace), MSA, Part II, Section 29-2.2.3.
 - 2) Total Carbon (Dry Combustion - High Temperature Induction Furnace), MSA, Part II, Section 29-2.2.4.
 - 3) Total Carbon (Dry Combustion - Other Instrument Methods), MSA, Part II, Section 29-2.2.5. Any other instrumentation, such as this, must be justified and provide results as

- precise and accurate as the results from Sections 29-2.2.3 and 29-2.2.4
- d) Total Carbon (Wet Digestion), MSA, Part II, Section 29-2.3.2 soil digested in 60:40 mixture of sulfuric acid and phosphoric acid (containing $K_2Cr_5O_7$). CO_2 evolved is absorbed and weighed, or absorbed in standard base and titrated. Specific examples are found in MSA, Part II, Figures 29-2 and 29-3, and Section 29-2.3.3.
 - e) Pre treatment prior to Dry combustion, MSA, Part II, Section 29-3.3.3. Inorganic Carbon is removed by treating sample in a combustion boat, with 5% sulfurous acid (H_2SO_3). After several hours, remove the excess H_2SO_3 by leaving overnight in an evacuated desiccator. Read citation for further details.
 - f) Pre treatment prior to Wet Combustion, MSA, Part II, Section 29-3.3.2. Inorganic Carbon is removed by sulfuric acid - ferrous sulfate reagent in apparatus used for Total Carbon (Wet Digestion) prior to Total Carbon measurement. See citation for further details.
 - g) Use only the methods specified above, or obtain approval of *region 5* CPMS, CRL prior to use of other method. Test procedure description, and description of specific measurement principals, including equivalency to each of the 10 items in Figure 29-1 of MSA, Part II and sample pre treatments of Section 29-3.
 - h) Laboratory performing Total Carbon determinations must have and use a recognized procedure for removal of any inorganic carbon in sample.
8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
 - a) A variety of apparatus, instruments, sample preparation systems and read-outs can be used. It is the responsibility of the laboratory to provide appropriate QC audits and QC data with each set of samples tested.
 - b) If instrumentation requires calibration, provide calibration curve, including zero concentration standard and preparation blanks. Provide positive control (a test sample prepared independently from calibration standards) that provides a measure of accuracy of the system. This should be done for all systems, including gravimetric read-outs.
 9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.):
 - a) As part of the Case Narrative, attach description of test procedures and instrumentation used for measurement of Total Carbon and removal of any inorganic carbon. Test procedure description must include sufficient information that the nature of specific analytical result deliverables can be

- determined, including QC audits. In the Case Narrative, discuss any problem type samples (including peat or muck soils), limitations on any sample results, and solutions taken to resolve any problems. A sample preparation log will be provided, as appropriate.
- b) Bench record tabulating any order of any sample weights and tare weights of absorbed CO₂, instrument calibrations, blanks, QA audits, etc., must be provided, along with copies of any worksheets used to calculate results. Include copies of any instrument readouts. All must be legible. Report results as % Carbon on a dry weight basis (103 - 105°C). Note that the analysis is performed on an air dried aliquot, but the results must be reported on a dry weight basis (103 - 105°C).

10. Other (use additional sheet(s) or attach supplementary information, as needed):

Data rejection and non payment will be recommended if the laboratory does not follow the methods referenced in this SAS. Lab must submit all original field documentation (COC's, tags, SAS PL's, etc.) and original data to Region in time frame referenced in Item 6 of this SAS (analogous to a RAS-CSF).

11. Name of sampling/shipping contact(s):

Tom Pachowicz / Cathy Sullivan - phone 312-663-9415

12. Data requirements:

<u>Parameter:</u>	<u>Detection Limit(s)</u>	<u>Precision Desired</u>
Total Organic Carbon (TOC) in Soil	0.10%	Difference in duplicate results should not exceed \pm 20% for concentrations $>2.0\%$ C or \pm 0.20% C for concentrations $<2.0\%$ C.

NOTE: These are minimum requirements. Report the actual detection limits used, based on the specified methodologies.

13. QC Requirements

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits*</u>
Prep. Blank	1 per group of 10 or fewer samples or at least twice.	$\leq 0.1\%$ C
Lab Duplicate	at least 1 per group of 5 or fewer samples.	$\leq 20\%$ RPD in duplicate sample results, or $< 0.2\%$ difference at small concentrations.
Positive Control (to be determined by the lab).	at least 1 per group of 10 or fewer samples.	88 - 115% Recovery
Instrument Calibration and Calibration Checks	1 per group of 10 or fewer samples.	90 - 110% recovery for calibration check, and $< 0.1\%$ C for assumed routine.
Blanks (if appropriate)	1 per group of 10 or fewer samples.	$< 1.0\%$ Carbon

14. Action required if limits are exceeded:

For corrective action and re analyze of samples - Contact SMO immediately.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Service. Should you have any questions, or need any assistance, please contact your Regional representative at the Sample Management Office.

APPENDIX C

CLP SAMPLE DOCUMENTATION AND CUSTODY PROCEDURES

SAMPLE DOCUMENTATION

Each sample processed by the CLP must be properly documented to ensure correct and complete analysis for parameters requested and to support the use of sample data in potential enforcement actions. The following sample documents may be required when shipping samples for RAS, RAS/SAS, or "ALL SAS" analysis to CLP laboratories or CRL. Document requirements are dependent on the analysis requested and the laboratory where the analysis is to be performed.

In addition to completing the sample forms, chain-of-custody (COC) and proper packaging and shipping procedures must be followed for each sample. The following topics will be discussed in this Appendix.

- o Maintaining Sample Custody
- o Sample Packaging Requirements
- o Sample Shipping Requirements
- o Sample Documents including
 - * Organic Traffic Report/Chain-of-Custody Form (OTR Combo Form).
 - * Inorganic Traffic Report/Chain-of-Custody Form (ITR Combo Form).
 - * SAS packing list/Chain-of-Custody Form (SAS Combo Form).
 - * CRL Sample Tracking Forms.
 - * Chain-of-Custody Record for CRL
 - * Sample Tag.
 - * Sample Label.
 - * Custody Seals.
 - * Federal Express Airbill.
 - * Sample Shipment Coordination Checklist.

Maintaining Sample Custody

In accordance with EPA enforcement requirements, official custody of samples must be maintained and documented from the time of collection until the required contract storage times have been met. Each cooler of samples shipped to a laboratory must be accompanied by a COC form or a COC Combo Form. This is the most important document that the sampler will complete in reference to the samples collected. It is imperative that it be filled out completely and correctly. If it is not, the integrity of all the samples listed can be called into question.

A sample is considered to be in an individual's custody if any of the following criteria are met:

1. The sample is in your possession or it is in your view after being in your possession;
2. It was in your possession and then locked up or sealed to prevent tampering; or
3. It is in a secured area. The site sampler is responsible for the care and custody of the collected samples until they are shipped.

When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record may document the transfer of custody of samples from the sampler to another person, to a mobile laboratory, to a permanent laboratory, to or from a secure storage area, or if samples are held overnight by the sampler, to the cooler itself.

The laboratory representative who accepts the incoming sample shipment signs and dates the COC record to acknowledge receipt of the samples. Once the sample transfer process is complete, the laboratory is responsible for maintaining internal logbooks and records that provide a custody record throughout the sample preparation and analysis.

Sample Packaging Requirements

Samples processed through the CLP and CRL must be package for shipment in compliance with current U.S. Department of Transportation (DOT) and commercial carrier regulations.

Water proof, metal or hard plastic ice chests or coolers are the only acceptable type of sample shipping container. Inside the cooler, sample containers must be enclosed in clear plastic bags so that sample tags and labels are visible. Strapping or filament tape must be placed around the seal of the sample container. With the exception of water VOA samples, all water sample levels must be marked with a wax pencil. Water and soil samples suspected to be of medium/high concentration, or soil samples suspected to contain dioxin must be enclosed in a metal can with a clipped or sealable lid (e.g. paint can). The outer metal can must be labeled with the number of the sample contained inside. Containers which do not fit into paint cans should be double bagged.

Shipping containers should be packed with non-combustible, absorbent packing material (e.g. vermiculite) surrounding the sample bottles or metal cans containing samples, to avoid breakage during transport. Cooler drainage plugs should be sealed closed with strapping tape to avoid leakage of melting ice inside the cooler. Ice in baggies should be used where appropriate to cool samples.

Paperwork accompanying the shipment must be enclosed in a waterproof plastic bag and taped to the underside of the cooler lid. Coolers must be labeled with visible address labels (including a return address) covered with clear tape, two custody seals (front right and back left) covered with clear tape, and THIS END UP/FRAGILE or other appropriate stickers on each side of each cooler.

Sample Shipping Requirements

All samples should be shipped through a reliable commercial carrier, such as Federal Express, Emery, Purolator, or the equivalent.

Sample shipper's offices are responsible for sample shipping charges.

Samples for organic analysis must be shipped for overnight delivery. If shipment requires more than a 24-hour period, sample holding times may be exceeded, compromising the integrity of the sample analysis.

One Federal Express Form must be filled out for each laboratory receiving sample coolers. The Federal Express Form should be filled out prior to arrival at a Federal Express station. In certain cases, Federal Express will be able to pick-up coolers from a designated area.

Sample Documents

Complete descriptions of how to fill out CLP and CRL sample paperwork follows.

THE ORGANIC TRAFFIC REPORT/CHAIN-OF-CUSTODY FORM (OTR Combo Form)

GENERAL

The OTR Combo form is used in conjunction with the shipment of samples to the EPA Contract lab for volatile, semi-volatile, and pesticide / PCB analysis. Each sample collected must be reported on this form in order to maintain chain-of-custody. It is important that the sampler indicate whether the sample shipment is complete or if there are more samples to be shipped to the lab under that case number.

DISTRIBUTION

Blue copy - Bring back to office.
Pink copy - Bring back to office.
White copy - Ship with samples.
Yellow copy - Ship with samples.

PREPARATION (See example)

1. Enter the Case number and SAS number if applicable; will be supplied by the SMC.
2. Project Code - enter the job number.
Regional Information - enter TFA 102.
Site Name - enter the site location.
Site Spill ID - enter if applicable.
3. Region No. - enter V.
Sampling Co. - enter E & E ARCS.
Sampler - enter your name.
Type of Activity - check the appropriate box.
4. Date Shipped - enter date samples were shipped.
Carrier - enter Federal Express.
Airbill No. - enter the appropriate number.
Ship to - enter the lab name, address, and contact person.
5. Enter the CLP Organic Sample Number.
 - A. Sample Description - enter appropriate description found in box 7 here. Enter sample description 4 (Rinsate) for blanks.
 - B. Concentration - enter appropriate concentration of the samples.
 - C. Comp/Grab - enter either composite or grab.

- D. Preservative - enter appropriate preservative for the analysis from box 6.
 - E. RAS Analysis - Check analysis desired.
 - F. Enter the tag numbers used on each bottle.
 - G. Station Location - enter the field location number (do not write dup, blank, or MSD here).
 - H. Enter date and time of sample collection.
 - I. Optional.
 - J. Enter the corresponding CLP inorganic sample numbers or the CRL tracking numbers.
 - K. Write field duplicate or field blank for the appropriate lines.
- 6. Circle Y or N depending on whether shipment is complete.
 - 7. Indicate the page number.
 - 8. Indicate the samples that are to be used for the MS/MSD.
 - 9. Additional sampler signature (optional).
 - 10. Enter the chain of custody seal numbers.
 - 11. Samplers signature and the date and time the samples are relinquished to the laboratory or shipping carrier.

[illegible]

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none



United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Organic Traffic Report & Chain of Custody Record

(For Organic CLP Analysis)

SAS No.
(if applicable)

NA

Case No

17524

1. Project Code LF3035	Account Code	2. Region No. V	Sampling Co. E&E ARCS	4. Date Shipped 1/7/92	Carrier Fed Ex
Regional Information TFA 102		Sampler (Name) Cathy Kouris		Airbill Number 3110833880	
Non-Superfund Program		Sampler Signature <i>Cathy Kouris</i>		5. Ship To PACE 1710 Douglas Drive Minneapolis, MN 55422 ATTN: Paul Ernst	
Site Name CONRAIL RAILYARD		3. Type of Activity			
City, State EIKHART, IN		Site Spill ID 7Y			
		Remedial SF <input checked="" type="checkbox"/> PA <input type="checkbox"/> ST <input type="checkbox"/> FED <input type="checkbox"/> Removal RIFS <input type="checkbox"/> RD <input type="checkbox"/> RA <input type="checkbox"/> O&M <input type="checkbox"/> NPLD <input type="checkbox"/> CLEM <input type="checkbox"/> REMA <input type="checkbox"/> REM <input type="checkbox"/> OIL <input type="checkbox"/> UST <input type="checkbox"/>			

6. Preservative
(Enter in Column D)
1. HCl
2. HNO₃
3. NaHSO₄
4. H₂SO₄
5. Other (SAS) (Specify)
6. Ice only
N. Not preserved

7. Sample Description
(Enter in Column A)
1. Surface Water
2. Ground Water
3. Leachate
4. Rinsate
5. Soil/Sediment
6. Oil (SAS)
7. Waste (SAS)
8. Other (SAS) (Specify)

CLP Sample Numbers (from labels)	A Enter # from Box 7	B Conc. Low Med High	C Sample Type: Comp / Grab	D Preservative from Box 6	E RAS Analysis				F Regional Specific Tracking Number or Tag Numbers	G Station Location Number	H Mo/Day/Year/Time Sample Collection	I Sampler Initials	J Corresp. CLP Inorg Samp. No	K Designated Field QC
					VOA	BNA	Pest/PCB	High ARO/TOX						
EPP17	5	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130626-28	B20C(5-65)	1/7/92 805		MEJK06	
EPP18	5	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130629-31	B20E(10-124)	1/7/92 830		MEJK07	
EPP19	5	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130632-35	B20E-D(10-124)	1/7/92 830		MEJK08	Field Duplicate
EPP20	5	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130636-38	B21(10-124)	1/7/92 915			
EPP21	2	L	G	1	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130639-40	CRMW115-01	1/7/92 1005		MEJK09	
EPP21	2	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130641-42	CRMW115-01	1/7/92 1005		MEJK09	
EPP22	2	L	G	1	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130643-44	CRMW115-01	1/7/92 1005		MEJK10	Field Duplicate
EPP22	2	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130645-46	CRMW115-01	1/7/92 1005		MEJK10	Field Duplicate
EPP23	4	L	G	1	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130647-48	CRMWFB-01	1/7/92 1115		MEJK11	Field Blank
EPP23	4	L	G	6	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		130649-50	CRMWFB-01	1/7/92 1115		MEJK11	Field Blank

Shipment for Case complete? (Y/N)

Page 1 of 1

Sample used for a spike and/or duplicate

EPP17, EPP21

Additional Sampler Signatures

Chain of Custody Seal Number

175654-55

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature) <i>Cathy Kouris</i>	Date / Time 1/7/92 1830	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none

THE INORGANIC TRAFFIC REPORT / CHAIN-OF-CUSTODY FORM (ITR Combo)

GENERAL

The ITR Combo form is used in conjunction with the shipment of samples to the EPA Contract Lab for total metals and cyanide analysis. Each sample collected must be reported on this form in order to maintain chain-of-custody. It is important that the sampler indicate whether the sample shipment is complete or if there are more samples to be shipped to the lab under that case number.

DISTRIBUTION

Green copy - Bring back to office.
Pink copy - Bring back to office.
White copy - Ship with samples.
Yellow copy - Ship with samples.

PREPARATION (See example)

1. Enter the Case number and SAS number if applicable; will be supplied by the SMC.
2. Project Code - enter the job number.
Regional Information - enter TFA 102.
Site Name - enter the name of the site.
City, State - enter the site location.
Site Spill ID - enter if applicable.
3. Region No. - enter V.
Sampling Co. - enter E & E ARCS.
Sampler - enter your name.
Type of Activity - check the appropriate box.
4. Date Shipped - enter date samples were shipped.
Carrier - enter Federal Express.
Airbill No. - enter the appropriate number.
Ship to - enter the lab name, address, and contact person.
5. Enter the CLP Inorganic Sample Number.
 - A. Sample Description - enter appropriate description found in box 7 here. Enter sample description 4 (Rinsate) for blanks.
 - B. Concentration - enter appropriate concentration of the samples.
 - C. Comp/Grab - enter either composite or grab.

- D. Preservative - enter appropriate preservative for the analysis from box 6.
 - E. RAS Analysis - Check analysis desired.
 - F. Enter the tag numbers used on each bottle.
 - G. Station Location - enter the field location number (do not write dup, blank, or MSD here).
 - H. Enter date and time of sample collection.
 - I. Optional.
 - J. Enter the corresponding CLP Organic sample numbers or the CRL tracking numbers.
 - K. Write field duplicate or field blank for the appropriate lines.
- 6. Circle Y or N depending on whether shipment is complete.
 - 7. Indicate the page number.
 - 8. Indicate the samples that are to be used for the MS/MSD.
 - 9. Additional sampler signature (optional).
 - 10. Enter the chain of custody seal numbers.
 - 11. Samplers signature and the date and time the samples are relinquished to the laboratory or shipping carrier.

Case No

[illegible]

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature) 11	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none



United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Inorganic Traffic Report & Chain of Custody Record

(For Inorganic CLP Analysis)

SAS No.
(if applicable)

Case No.

N/A

17524

1. Project Code ZF3035	Account Code	2. Region No. IV	Sampling Co. E&E ARCS	4. Date Shipped 1/7/92	Carrier Fed Ex	6. Preservative (Enter in Column D) 1. HCl 2. HNO ₃ 3. NaOH 4. H ₂ SO ₄ 5. K ₂ Cr ₂ O ₇ 6. Ice only 7. Other (SAS) (Specify) N. Not preserved	7. Sample Description (Enter in Column A) 1. Surface Water 2. Ground Water 3. Leachate 4. Rinsate 5. Soil/Sediment 6. Oil (SAS) 7. Waste (SAS) 8. Other (SAS) (Specify)									
Regional Information TEA 102 Non-Superfund Program		Sampler (Name) Cathy Kouris Sampler Signature <i>Cathy Kouris</i>		Airbill Number 3110833891												
Site Name CONRAIL RAILYARD		4. Type of Activity SF <input checked="" type="checkbox"/> PRP <input type="checkbox"/> ST <input type="checkbox"/> FED <input type="checkbox"/> PA <input type="checkbox"/> SSI <input type="checkbox"/> LSI <input type="checkbox"/> Remedial RIFS <input checked="" type="checkbox"/> RD <input type="checkbox"/> RA <input type="checkbox"/> O&M <input type="checkbox"/> NPLD <input type="checkbox"/> Removal CLEM <input type="checkbox"/> REMA <input type="checkbox"/> REM <input type="checkbox"/> OIL <input type="checkbox"/> UST <input type="checkbox"/>		5. Ship To KEYTX 8300 West PARK DR. HOUSTON, TX 77063 ATTN: Dela MASSOUDI												
City, State EIKHART, IN	Site Spill ID 7Y	CLP Sample Numbers (from labels)		A Enter # from Box 7	B Conc. Low Med High	C Sample Type: Comp / Grab	D Preservative from Box 6	E - RAS Analysis Metals: Total <input checked="" type="checkbox"/> Dissolved <input checked="" type="checkbox"/> Cyanide <input checked="" type="checkbox"/> Nitrate <input checked="" type="checkbox"/> Nitrite <input checked="" type="checkbox"/> Fluoride <input checked="" type="checkbox"/> pH <input checked="" type="checkbox"/> Conductivity <input checked="" type="checkbox"/>		F Regional Specific Tracking Number or Tag Numbers	G Station Location Number	H Mo/Day/Year/Time Sample Collection	I Sampler Initials	J Corresp. CLP Org. Samp. No.	K Designated Field QC	
MEJK06	5	L	G	N	X	X				130709	B20C(5-6.5M)	1/7/92 805	EPP17			
MEJK07	5	L	G	N	X	X				130710	B20E(10-12M)	1/7/92 830	EPP18			
MEJK08	5	L	G	N	X	X				130711	B20E(10-12M)	1/7/92 830	EPP19			Field Duplicate
MEJK09	2	L	G	2	X					130712	CRMW115-01	1/7/92 1005	EPP21			
MEJK09	2	L	G	3		X				130713	CRMW115-01	1/7/92 1005	EPP21			
MEJK10	2	L	G	2	X					130714	CRMW115-01	1/7/92 1005	EPP22			Field Duplicate
MEJK10	2	L	G	3		X				130715	CRMW115-01	1/7/92 1005	EPP22			Field Duplicate
MEJK11	4	L	G	2	X					130716	CRMWFB-01	1/7/92 1115	EPP23			Field Blank
MEJK11	4	L	G	3		X				130717	CRMWFB-01	1/7/92 1115	EPP23			Field Blank
Shipment for Case complete? (Y/N) (N)		Page 1 of 1	Sample used for a spike and/or duplicate MEJK06, MEJK09		Additional Sampler Signatures		Chain of Custody Seal Number 175658-59									

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature) <i>Cathy Kouris</i>	Date / Time 1/7/92 1830	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none

SAS PACKING LIST / CHAIN-OF-CUSTODY FORM (SAS Combo Form)

GENERAL

The SAS Combo form is used in conjunction with the shipment of samples to the CLP laboratories for "all SAS" analysis. Each sample collected must be reported on this form in order to maintain chain-of-custody. It is important that the sampler indicate whether the sample shipment is complete or if there are more samples to be shipped to the lab under that case number. SAS Combo forms are used in place of OTR and ITR Combo forms.

DISTRIBUTION

White copy - Bring back to office.
Yellow copy - Bring back to office.
Gold copy - Ship with samples.
Pink copy - Ship with samples.

PREPARATION (See example)

1. Enter the SAS number; will be supplied by the SMC.
2. Project Code - enter the job number.
Regional Information - enter TFA 102.
Site Name - enter the name of the site.
City, State - enter the site location.
Site Spill ID - enter if applicable.
3. Region No. - enter V .
Sampling Co. - enter E & E ARCS.
Sampler - enter your name.
Type of Activity - check the appropriate box.
4. Date Shipped - enter date samples were shipped.
Carrier - enter Federal Express.
Airbill No. - enter the appropriate number.
Ship to - enter the lab name, address, and contact person.
5. Enter the SAS sample numbers.
 - A. Sample Description - enter appropriate description found in box 7 here. Enter sample description 4 (Rinsate) for blanks.
 - B. Concentration - enter appropriate concentration of the samples.
 - C. Preservative - enter appropriate preservative for the analysis from box 6.

- D. Analysis - enter the type of analysis.
 - E. Enter the tag numbers used on each bottle.
 - F. Station Location - enter the field location number (do not write dup, blank, or MSD here).
 - G. Enter date and time of sample collection.
 - H. Optional.
 - I. Write field duplicate or field blank for the appropriate lines.
- 6. Circle Y or N depending on whether shipment is complete.
 - 7. Indicate the page number.
 - 8. Indicate the samples that are to be used for the MS/MSD.
 - 9. Additional sampler signature (optional).
 - 10. Enter the chain of custody seal numbers.
 - 11. Samplers signature and the date and time the samples are relinquished to the laboratory or shipping carrier.



United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Special Analytical Service

Packing List/Chain of Custody

SAS No.

1

1. Project Code	Account Code	2. Region No.	Sampling Co.	4. Date Shipped	Carrier	6. Sample Description (Enter in Column A) 1. Surface Water 2. Ground Water 3. Leachate 4. Rinsate 5. Soil/Sediment 6. Oil 7. Waste 8. Other (Specify)	7. Preservative (Enter in Column C) 1. HCl 2. HNO ₃ 3. NaHSO ₄ 4. H ₂ SO ₄ 5. NaOH 6. Other (SAS) (Specify) 7. Ice only N. Not preserved		
Regional Information		Sampler (Name)		Airbill Number	4				
Non-Superfund Program 2		Sampler Signature 3		5. Ship To					
Site Name		3. Type of Activity							
City, State		Site Spill ID							
		3. Type of Activity							
		Lead Pre-Remedial RIFS Remedial Removal							
		SF <input type="checkbox"/> PA <input type="checkbox"/> RA <input type="checkbox"/> CLEM <input type="checkbox"/>							
		PRP <input type="checkbox"/> SS <input type="checkbox"/> O&M <input type="checkbox"/> REM <input type="checkbox"/>							
		ST <input type="checkbox"/> LSI <input type="checkbox"/> NPLD <input type="checkbox"/> OIL <input type="checkbox"/>							
		FED <input type="checkbox"/> UST <input type="checkbox"/>							
Sample Numbers	A Matrix Enter from Box 6	B Conc Low Med High	C Preservative Used from Box 7	D Analysis	E Regional Specific Tracking Number or Tag Number	F Station Location Identifier	G Mo/Day/Year/Time Sample Collection	H Sampler Initials	I Designated Field QC
1.									
2.									
3.									
4. 5									
5.									
6.									
7.									
8.									
9.									
10.									
Shipment for SAS complete? (Y/N) 6		Page 1 of 7	Sample Used for Spike and/or Duplicate 8		Additional Sampler Signatures 9		Chain of Custody Seal Number 10		

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature) 11	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none



United States Environmental Protection Agency
Contract Laboratory Program Sample Management Office
PO Box 818 Alexandria, VA 22313
703-557-2490 FTS 557-2490

Special Analytical Service

Packing List/Chain of Custody

SAS No.

6922E

1. Project Code ZF3035		Account Code		2. Region No. V		Sampling Co. E&E ARCS		4. Date Shipped 1/7/92		Carrier Fcd Ex		6. Sample Description (Enter in Column A)		7. Preservative (Enter in Column C)		
Regional Information TFA 102				Sampler (Name) Cathy Kouris				Airbill Number 3110834053				1. Surface Water 2. Ground Water 3. Leachate 4. Rinsate 5. Soil/Sediment 6. Oil 7. Waste 8. Other (Specify) 1. HCl 2. HNO3 3. NAHSO4 4. H2SO4 5. NaOH 6. Other (SAS) (Specify) 7. Ice only N. Not preserved				
Non-Superfund Program				Sampler Signature Cathy Kouris				5. Ship To CENTEC 1401 Municipal Rd Roanoke, VA 24012								
Site Name CONRAIL RAILYARD				3. Type of Activity				ATTN: B HUTCHENSON								
City, State EIKHART, IN				Site Spill ID 7Y												
Sample Numbers		A Matrix Enter from Box 6	B Conc Low Med High	C Preserv- ative Used from Box 7	D Analysis		E Regional Specific Tracking Number or Tag Number		F Station Location Identifier		G Mo/Day/ Year/Time Sample Collection		H Sampler Initials		I Designated Field QC	
1. E-01		2	L	7	BOD		130759		CRMW025-02		1/7/92 1005					
2. E-01		2	L	4	COD		130760		CRMW025-02		1/7/92 1005					
3. E-02		2	L	7	BOD		130761		CRMW025-02D		1/7/92 1005				Field Dup	
4. E-02		2	L	4	COD		130762		CRMW025-02D		1/7/92 1005				Field Dup	
5. E-03		2	L	7	BOD		130763		CRMW235-01		1/7/92 1115					
6. E-03		2	L	4	COD		130764		CRMW235-01		1/7/92 1115					
7. E-04		2	L	7	BOD		130765		CRMW01B-01B		1/7/92 1300				Field Blank	
8. E-04		2	L	4	COD		130766		CRMW01B-01B		1/7/92 1300				Field Blank	
9.																
10.																
Shipment for SAS complete? (Y/N)		Page 1 of 1		Sample Used for Spike and/or Duplicate E-03				Additional Sampler Signatures				Chain of Custody Seal Number 175672-73				

CHAIN OF CUSTODY RECORD

Relinquished by: (Signature) Cathy Kouris	Date / Time 1/7/92 1830	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Received by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	Is custody seal intact? Y/N/none

CRL SAMPLE TRACKING FORMS

GENERAL

The CRL Tracking forms are used in conjunction with the shipment of samples to the EPA CRL lab. The tracking forms will be given to the sampler by the SMC. CRL Tracking forms must be accompanied by a Chain-of-Custody form.

DISTRIBUTION

All Tracking forms are sent to the EPA lab with the shipment.

PREPARATION: (See example)

1. Division/Branch: ARCS.
2. Sampling Date: Self-explanatory (sampler will fill in).
3. Lab Arrival Date: This will be the next day if sent via Federal Express; or whenever samples are scheduled to arrive at the lab (sampler will fill in).
4. Due Date: Count 21 days including lab arrival date and weekends. If due date falls on a weekend, the following Monday should be used instead (sampler will fill in.)
5. DU Number: Leave blank.
6. Data Set Number: Leave blank.
7. Study: Site name.
8. Priority: Leave blank.
9. Contractor: Ecology and Environment.
10. CRL Numbers: 92ZE01S09, R08, D09
92 - Fiscal year.
ZE - ARCS Code.
01 - The first sequence of numbers in first series of 100 sample numbers.
S09 - The ninth sample assigned in the first series of 100 samples.

R08 - The eighth blank assigned in the first series of 100 samples.

D09 - Duplicate of sample assigned number S09.

11. Sample Description: Whatever is appropriate description of the sample location (CRMW11S-01, FB01).
12. Analysis: SMC will check appropriate analysis.
13. Duplicate Sample: Enter the last 2 digits of the sample where the duplicate was collected (sampler will fill in).

Write in at the bottom whether the shipment is complete.

DIVISION/BRANCH 1 SAMPLE DATE 2 LAB ARRIVAL DATE 3 DUE DATE 4
 DU NUMBER 5 DATA SET NUMBER 6 STUDY 7 PRIORITY 8 CONTRACTOR 9

[illegible]

DIVISION/BRANCH ARCS SAMPLE DATE 1/7/92 LAB ARRIVAL DATE _____ DUE DATE _____
DU NUMBER _____ DATA SET NUMBER — STUDY CONRAIL RAILROAD PRIORITY — CONTRACTOR — E&E

20

DIVISION/BRANCH ARCS SAMPLE DATE 1/7/92 LAB ARRIVAL DATE 1/8/92 DUE DATE 1/28/91
PROJECT NUMBER DATA SET NUMBER — STUDY CONRAIL RAILROAD PRIORITY — CONTRACTOR — E&E

[illegible]

CHAIN-OF-CUSTODY RECORD FOR CRL

GENERAL:

A Chain-of-Custody form must be completed for each cooler shipped.

DISTRIBUTION:

- | | |
|------------------------|-------------------------|
| 1. First copy (white) | - Ship with samples. |
| 2. Second copy (pink) | - Bring back to office. |
| 3. Third copy (yellow) | - Bring back to office. |

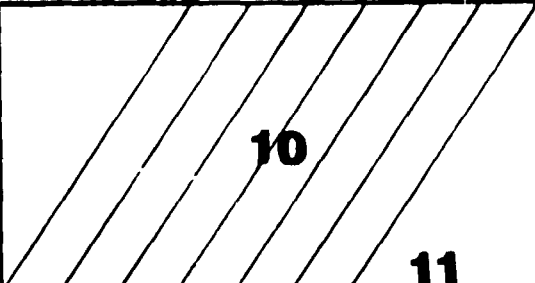
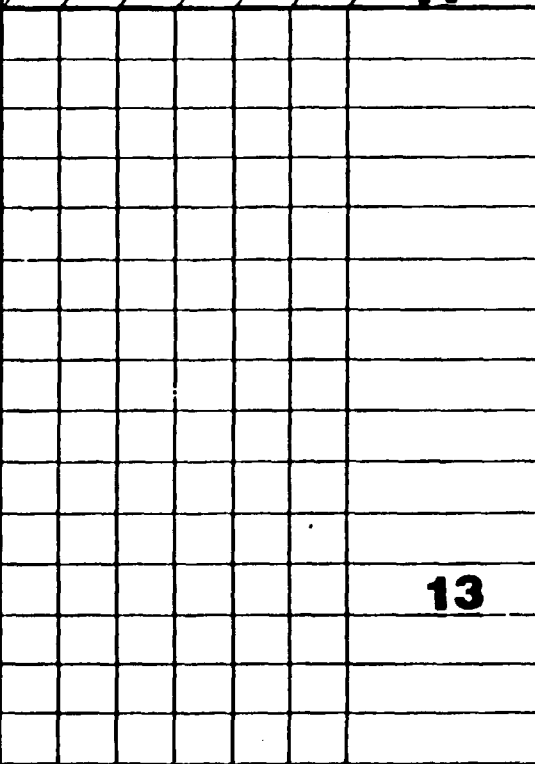
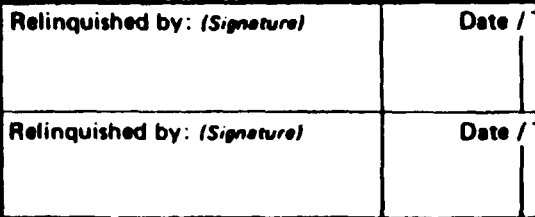
PREPARATION: (See example)

- | | |
|-------------------------------------|--|
| 1. Project Number | - Enter Job # |
| 2. Project Name | - Enter Site Name. |
| 3. Samplers | - Enter signatures of all samplers who have signed sample tags. |
| 4. Station Number | - Enter CRL numbers. |
| 5. Date | - Enter sampling date. |
| 6. Time | - Enter sampling time; use military time. |
| 7. Comp/Grab | - Check if sample is composite or grab. |
| 8. Station Location | - Enter sample location description which must match that on tags and CRL forms (CRMW11S-01, FB01). |
| 9. Number of Containers | - Enter number of containers collected at each station number. |
| 10. Inside Slanted Lines | - Enter volume and parameters (include preservatives as appropriate). |
| 11. Remarks | - Enter tag numbers. |
| 12. Sample Matrix/
Concentration | - Indicate sample matrix and Concentration. |
| 13. CRL Tracking Forms | - Add cooler number and which cooler number the CRL Tracking forms are in, as appropriate. |
| 14. Metals Filtered | - If the Chain-of-Custody is for monitoring wells, indicate whether metals have or have not been filtered. |
| 15. Relinquished by | - Samplers signature and the date and Date/Time time the samples are relinquished to laboratory or shipping carrier. |
| 16. Remarks (lower | - Enter method of shipment, laboratory right-hand corner) shipped to (may use acronym), airbill number and custody seal numbers. |

ENVIRONMENTAL PROTECTION AGENCY
Office of Enforcement

SECTION 5
230 South Dearborn Street
Chicago, Illinois 60604

CHAIN OF CUSTODY RECORD

PROJ. NO. 1		PROJECT NAME 2				NO OF CON- TAINERS	 10										REMARKS	
SAMPLERS: (Signature) 3																		
STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION													
4	5	6	7	8	9	 11										12		
						 13										14		
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Relinquished by: (Signature)		Date / Time		Received by: (Signature)								
15																		
Relinquished by: (Signature)		Date / Time		Received by: (Signature)		Relinquished by: (Signature)		Date / Time		Received by: (Signature)								
Relinquished by: (Signature)		Date / Time		Received for Laboratory by: (Signature)		Date / Time		Remarks										
								16										

Cooler #107

[illegible]

SAMPLE TAG

GENERAL:

A sample tag is completed for every sample collected and attached to the sample container.

PREPARATION: (See example)

1. Case or Project Code - Enter Job #.
2. Sample Number - Enter sample point (station) number; must match locations on C.O.C.
3. Month/Day/Year - Self explanatory.
4. Time - Use military time.
5. Designate - Comp (Composite) or grab (Check only one).
6. Station Number/Location - Enter sample point (station) number.
7. Samplers - Enter signature of sampler.
8. Preservative - Check as appropriate; if "other" is checked, preservative must be written in.
9. Analysis - Check analysis desired.
10. Remarks - Enter Traffic Report number or SAS sample number (if applicable). The Case number and/or SAS number should be written here also.
11. MS/MSD - Check as appropriate.

Case # or Project Code 1	Sample Number 2	Month/Day/Year 3	Time 4	DESIGNATE	
				Comp	Grab 5
Station Number and Location 6 Tag Number 5-198823		Samplers (signatures) 7			
PRESERVATIVE: H ₂ SO ₄ <input type="checkbox"/> HCL <input type="checkbox"/> HNO ₃ <input type="checkbox"/> NaOH <input type="checkbox"/> Other <input type="checkbox"/> 8					
ANALYSES					
VOA		METALS			
ABN		CYANIDE			
PEST/PCB		9			
Pesticides		Mercury			
Herbicides		Fluoride			
PCB		TOC			
PCDD/PCDF		BOD			
2,3,7,8-TCDD		COB			
Ames Mutagen		TDS			
Asbestos		TSS			
Phosphorus		O&G			
TO1		Sulfate			
TO2		Chloride			
TOX		Sulfide			
CBOD		Ammonia			
Bio-Acute		Alkalinity			
Bio-Chronic		Acidity			
Bio-Chronic		TKN			
Remarks: 10					
USE FOR MS/MSD <input type="checkbox"/> 11 Lab Sample Number					

Case # or Project Code ZF3035	Sample Number CRMW115-01	Month/Day/Year 1/7/92	Time 1005	DESIGNATE	
				Comp.	Grab <input checked="" type="checkbox"/>
Station Number and Location CRMW115-01 Tag Number 5-198824		Samplers (signatures) Cathy Kouris			
PRESERVATIVE: H ₂ SO ₄ <input type="checkbox"/> HCL <input type="checkbox"/> HNO ₃ <input checked="" type="checkbox"/> NaOH <input type="checkbox"/> Other <input type="checkbox"/>					
ANALYSES					
VOA		METALS			
ABN		CYANIDE			
PEST/PCB					
Pesticides		Mercury			
Herbicides		Fluoride			
PCB		TOC			
PCDD/PCDF		BOD			
2,3,7,8-TCDD		COB			
Ames Mutagen		TDS			
Asbestos		TSS			
Phosphorus		O&G			
TO1		Sulfate			
TO2		Chloride			
TOX		Sulfide			
CBOD		Ammonia			
Bio-Acute		Alkalinity			
Bio-Chronic		Acidity			
Bio-Chronic		TKN			
Remarks: CASE:17524 MEK 09					
USE FOR MS/MSD <input type="checkbox"/> Lab Sample Number					

SAMPLE LABEL

GENERAL:

A sample label is completed for every sample collected and attached to the sample container.

PREPARATION: (See example)

1. Date - Enter date of sample collection in top left-hand corner of label.
2. Sample Number - Enter the sample point (station) number (CRMW11S-01, FB01); must match locations on sample tag and C.O.C.
3. Time - Enter time (military format) in top right-hand corner of label.
4. Traffic Report Number - Enter either the CLP or CRL Traffic Report Number, or the SAS number in the center of the label, and the analysis to be performed (i.e. EKE24-VOA).

1

2

3

4

1/7/92 CRMW115-01 1245

EPL99 - VOA

1/7/92 CRMW115-01 1245

MEKJ63 - TOTAL METALS

1/7/92 CRMW115-01-1245

92ZE22510 - Rest/PCB

1/7/92 CRMW115-01 1245

6864E-03 - Oil & GREASE

CUSTODY SEALS

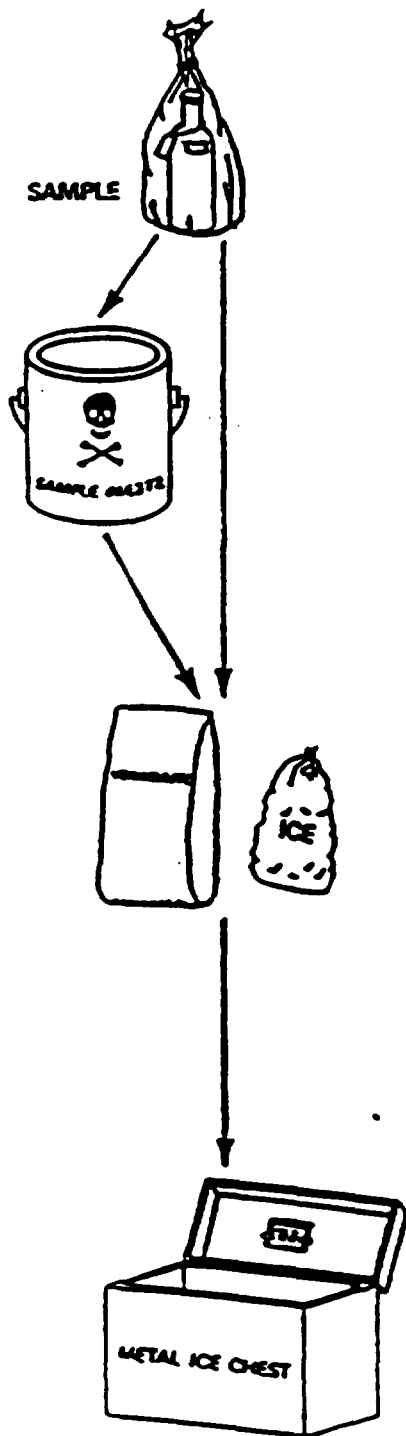
All coolers containing samples must be sealed with 2 custody seals. The custody seals are placed on the front and back edges of the cooler in such a manner that attempts to open the cooler will cause damage to the seal. Clear tape must cover the custody seals.

**U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
OFFICIAL SEAL
No 172474**

MAXIMUM NUMBER OF BOTTLES OR SAMPLES PER COOLER

	54-quart cooler	80-quart cooler	100-quart cooler
80 oz.	6 bottles	8 bottles	10 bottles
1 liter amber	9 bottles	12 bottles	16 bottles
1 liter plastic	16 bottles	20 bottles	26 bottles
2-120 ml and 1-8 oz. (for organic soil samples)	8 samples	11 samples	15 samples
1 - 8 oz. (for inorganic soil samples)	15 samples	21 samples	27 samples
2413:1			

SAMPLE PACKAGING SUMMARY

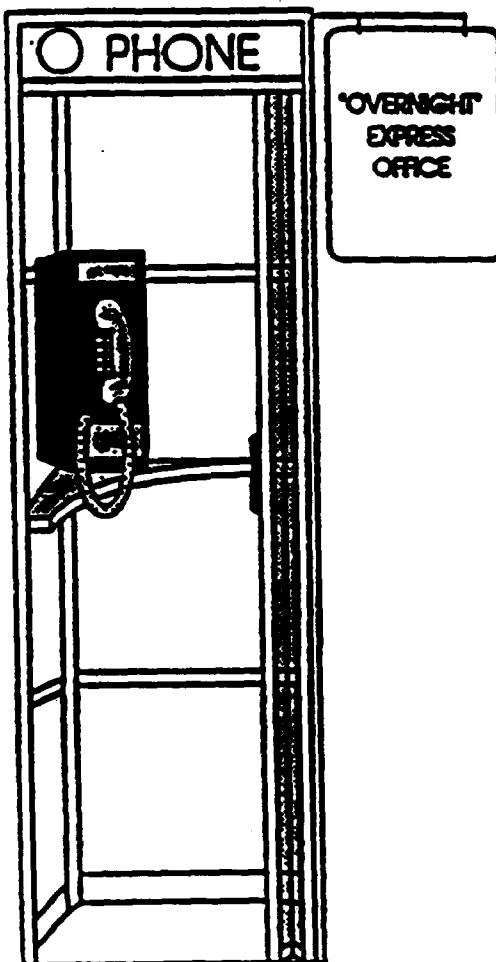


- ENCLOSE ALL SAMPLE CONTAINERS IN CLEAR PLASTIC BAGS.
- PACK ALL MEDIUM AND HIGH LEVEL WATER AND SOIL SAMPLES IN METAL PAINT CANS.
- LABEL PAINT CANS WITH SAMPLE NUMBER OF SAMPLE CONTAINED INSIDE.
- SURROUND CONTENTS OF CAN WITH NON-COMBUSTIBLE, ABSORBENT PACKING MATERIAL.
- USING FREEZER PACKAGES OR ICE SEALED IN PLASTIC BAGS, COOL ORGANIC LOW OR MEDIUM SAMPLES AND INORGANIC SAMPLES TO BE ANALYZED FOR CYANIDE TO 4°C.
- ICE IS NOT REQUIRED IN SHIPPING LOW LEVEL SOIL SAMPLES, BUT MAY BE UTILIZED AT THE DISCRETION OF THE SAMPLER.
- DO NOT COOL DIOXIN, INORGANIC LOW LEVEL WATER, INORGANIC MEDIUM/HIGH LEVEL WATER OR SOIL, OR ORGANIC HIGH LEVEL WATER OR SOIL SAMPLES.
- PACK SEALED PAINT CANS OR PLASTIC-ENCLOSED SAMPLE BOTTLES IN SHIPMENT CONTAINER.
- USE A METAL ICE CHEST FOR SHIPMENT (DO NOT USE CARDBOARD OR STYROFOAM CONTAINERS TO SHIP SAMPLES).
- SURROUND CONTENTS WITH NON-COMBUSTIBLE, ABSORBENT PACKING MATERIAL (DO NOT USE EARTH OR ICE PACKING MATERIALS).
- TAPE PAPERWORK IN PLASTIC BAGS UNDER COOLER LID.
- CLOSE COOLER AND SEAL WITH CUSTODY SEALS.

SAMPLE SHIPMENT COORDINATION CHECKLIST

Upon shipment of samples, samplers
must notify the SMC at E&E at (312)663-9415
or SMO at (703)684-5678 or (703)557-2490
Before 10:00am on the day after shipment.

Be prepared to give the
following information:



- ☞ Site name/Case/SAS
- ☞ Number and matrices
(soil, water, etc.)
of samples shipped
- ☞ Names of Laboratories
- ☞ Number of coolers
shipped per lab
- ☞ Shipping date
- ☞ Carrier, Airbill numbers
- ☞ Information on whether
shipment is complete or not,
Changes, Delays, Continuations,
Etc., pertaining to the case
- ☞ Sampler's name,
region, Phone#

SMO must be notified by 3:00pm friday for samples
intended for saturday delivery/pickup.

FEDERAL EXPRESS AIRBILL

GENERAL:

All samples collected will either be hand delivered to the lab by the sampler or will be shipped to the lab by Federal Express. To insure timely delivery of the samples, the Federal Express Airbill must be completed correctly.

DISTRIBUTION:

The shipper's copy (pink) of the airbill must be retained by the sampler at the time of shipment. This copy is given to the Cost Analyst.

All other copies of the airbill are retained by Federal Express.

PREPARATION:

An Example of a Federal Express Airbill and a Federal Express Dangerous Goods Airbill are shown on the following pages.

One airbill should be filled out per lab.

SAMPLE SHIPMENT REQUIREMENTS

Unanalyzed samples that potentially contain hazardous substances are packaged and shipped according to DOT or IATA regulations. If a compound is known to be present in a sample, the samples should be shipped as stated in the DOT Hazardous Material Table (49 CFR 172.101) or the IATA Hazardous Material Table. (see the regulations in the corporate library or the shipping guides in the SMC's office)



USE THIS AIRBILL FOR DANGEROUS GOODS SHIPMENTS ONLY IF THE SHIPPER IS A U.S. AIRCRAFT PASSENGER.
USE THE INTERNATIONAL AIRWAYBILL FOR SHIPMENTS TO PUERTO RICO AND ALL NON U.S. LOCATIONS.
QUESTIONS? CALL 800-238-5355 TOLL FREE.

TRACKING NUMBER

UC0C60C 10U

282M

0282682960



Sender's Federal Express Account Number

1270-9910-3

Date 1/7/91

From (Your Name) Please Print

Cathy Kouris

Company

ECOLOGY & ENVIRONMENT

Street Address

7030 N. Milwaukee Ave.

City

Niles

State

IL

ZIP Required

60648

Your Phone Number (Very Important)

708,649-1713

Department / Floor No

To (Recipient's Name) Please Print

B. HUTCHENSON

Company

CEN TEC

Exact Street Address (We Cannot Deliver to P.O. Boxes or P.O. Zips Only)

1401 MUNICIPAL Rd

ROANOKE

State

VA

Recipient's Phone Number (Very Important)

416-822-1111

Department / Floor No

YOUR INTERNAL BILLING REFERENCE INFORMATION (First 24 characters and appear on invoice)

ZF3035-05.24

IF HOLD FOR PICK-UP, Print FEDEX Address Here (Not available at all locations)

PAYMENT 1 ☒ Bill Sender 2 ☐ Bill Recipient's FedEx Acct No 3 ☐ Bill 3rd Party FedEx Acct No 4 ☐ Bill Credit Card

5 ☐ Cash/Check 6 ☐ Credit Card No

SERVICES (Check only one box)

Priority Overnight Service

Standard Overnight Service

Second Day Air Service

Heavyweight Service

Next Business Day Air Service

Next Business Day Air Service

Next Business Day Air Service

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DELIVERY AND SPECIAL HANDLING (Check services required)

1 ☐ HOLD FOR PICK-UP (48 hr. max)

2 ☒ DELIVER WEEKDAY

3 ☐ DELIVER SATURDAY (Extra charge)

4 ☒ DANGEROUS GOODS (Extra charge)

5 ☐ DRY ICE

6 ☐ OTHER SPECIAL SERVICE

7 ☐ OTHER SPECIAL SERVICE

8 ☐ OTHER SPECIAL SERVICE

9 ☐ OTHER SPECIAL SERVICE

10 ☐ OTHER SPECIAL SERVICE

11 ☐ OTHER SPECIAL SERVICE

12 ☐ HOLIDAY DELIVERY (in chosen date range)

INSTRUCTIONS (Mark appropriate boxes)

• Dangerous Goods as per attached Shipper's Declaration ☐

• Dangerous Goods Shipper's Declaration not required ☐

• Cargo Aircraft only ☐

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0282682960

AIRBILL NUMBER

SHIPPER'S CERTIFICATION FOR RESTRICTED ARTICLES/DANGEROUS GOODS

CHECK ONE ☐ 49 CFR

☒ IATA/ICAO

(TYPE OR PRINT)

DANGEROUS GOODS IDENTIFICATION		UN OR ID NO	SUBS-DIVISION	QUANTITY AND TYPE OF PACKING	PACKING NET	AUTHORIZATION
PROPER SHIPPING NAME	CLASS OR DIVISION					
OTHER Regulated substance Solid, N.O.S. (ENVIRONMENTAL Samples)	9	ID8027	-	PG III 1 PKG CONTAINING 34 X 8oz Bottles in CANS	906	

ADDITIONAL HANDLING INFORMATION

INSIDE CONTAINERS comply with prescribed Regulations / PASSENGER AIRCRAFT

TRANSPORT DETAILS	THIS SHIPMENT IS WITHIN THE LIMITATIONS PRESCRIBED FOR	PASSENGER AIRCRAFT	CARGO AIRCRAFT ONLY	(DELETE-NONAPPLICABLE)
AIRPORT OF DEPARTURE	AIRPORT OF DESTINATION	SHIPMENT TYPE	NON-RADIOACTIVE	RADIOACTIVE

IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS OR TREATMENT.

I HEREBY DECLARE THAT THE CONTENTS OF THIS CONSIGNMENT ARE FULLY AND ACCURATELY DESCRIBED ABOVE BY PROPER SHIP NAME AND ARE CLASSIFIED, PACKED, MARKED, AND LABELED, AND ARE IN ALL RESPECTS IN PROPER CONDITION FOR TRANSPORT BY ACCORDING TO THE APPLICABLE INTERNATIONAL AND NATIONAL GOVERNMENT REGULATIONS.

NAME AND TITLE OF SHIPPER

Cathy Kouris - ENVIRONMENTAL Sampler 242 Ross, Elkhart, IN 46344

EMERGENCY TELEPHONE NUMBER

312-663-9415

SIGNATURE OF SHIPPER

Cathy Kouris

SEE WARNING ON BACK